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**46th**

**THE OHIO STATE UNIVERSITY
INTERNATIONAL SYMPOSIUM ON
MOLECULAR SPECTROSCOPY
JUNE 17-21, 1991**

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INFORMATION

ACCOMMODATIONS: The check-in for dormitory accommodations is located in Drackett Tower (F) on Carl Drive.

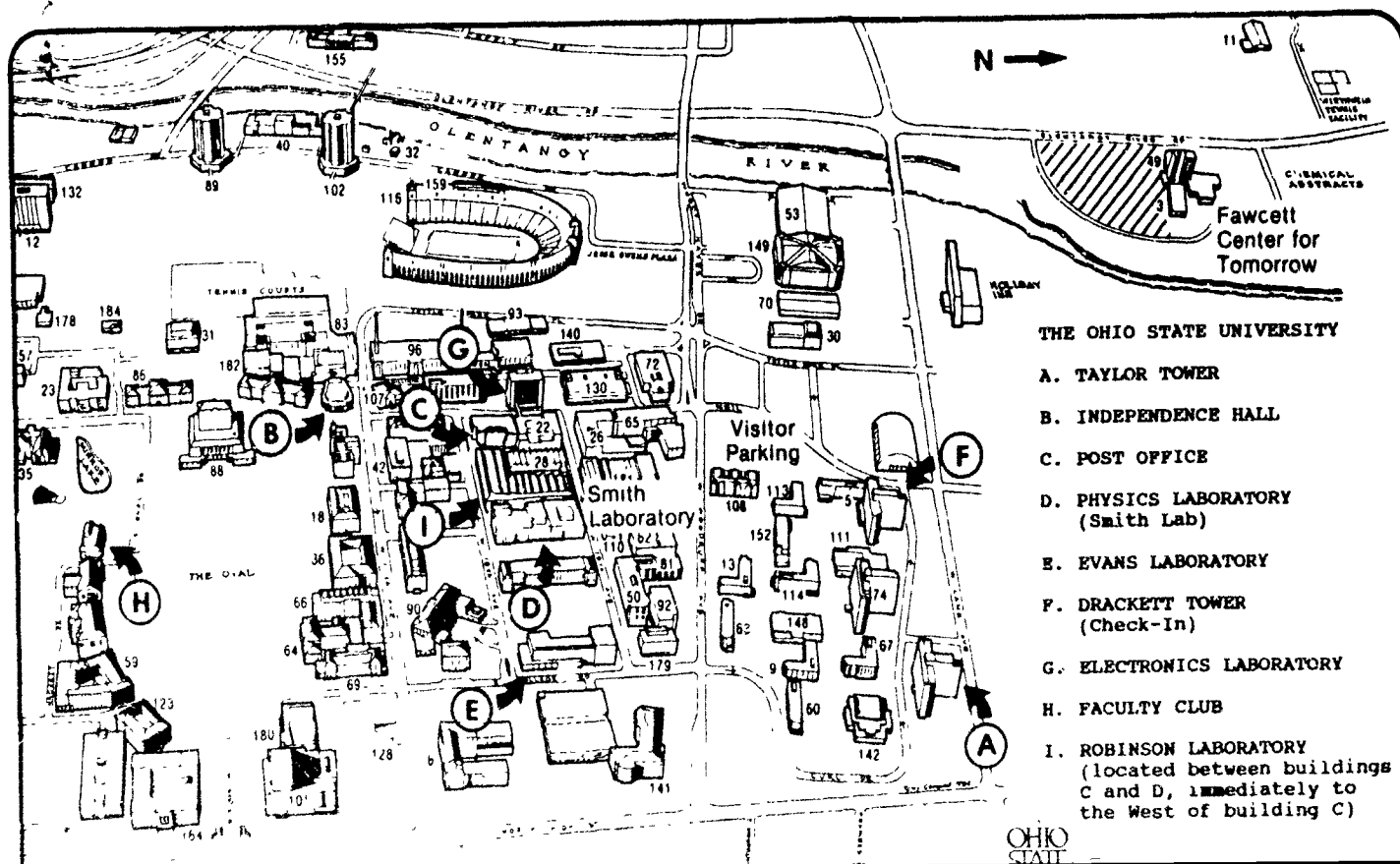
BANQUET: This will take place at the Ohio State University Faculty Club (H) on Wednesday, June 19, 1991, at 7:00 p.m. preceded by a reception starting at 6:00 p.m. Prof. Takeshi Oka, Robert A. Milliken Distinguished Service Professor of the University of Chicago will speak on "ASTRONOMY AND SPECTROSCOPY".

MAIL: Address your mail for delivery during the Symposium to: c/o MOLECULAR SPECTROSCOPY SYMPOSIUM, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, Ohio, 43210, U.S.A.

PARKING: Please purchase your parking permits when you check into the dorms or at the Registration Desk. These permits allow you to park in the Tuttle-Woodruff parking lot only. The permits must be displayed on the front windshield of your car. Please follow all traffic rules to avoid the issuance of tickets.

REGISTRATION: The Registration Desk will be located in Room 1036, Physics Laboratory. It will be kept open between 8:30 a.m. - 12 n and 1:00 - 4:30 p.m., Monday through Friday. The registration fee is \$65.00 per participant and \$55.00 if paid by May 10. The special rate of \$25.00 per Graduate Student will be reduced to \$20.00 if paid by May 10.

SESSIONS: They will be held in: Independence Hall (B), Physics Lab (D), and Evans Chemical Lab (E). Letters in parentheses correspond to the campus map below:



REPORT DOCUMENTATION PAGE

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MONDAY, JUNE 17, 1991 -- 8:45 A.M.

Auditorium, Independence Hall

Chair before Intermission: FRANK C. DE LUCIA, Department of Physics,
The Ohio State University, Columbus, Ohio.

Chair After Intermission: RACHAEL BARBOUR, BP Research, Cleveland, Ohio;
and President, Coblenz Society.

Plenary Session

- MA1. STRATOSPHERIC SPECTROSCOPY: UARS AND BEYOND.....35 min.
(UARS = Upper Atmospheric Research Satellite)

HERBERT M. PICKETT, Jet Propulsion Laboratory, California
Institute of Technology, Pasadena, California, 91109.

- MA2. MILLIMETER AND SUBMILLIMETER WAVE SPECTROSCOPY OF REACTIVE
SPECIES.....35 min.

CLAIRE DEMUYNCK, Laboratoire de Spectroscopie Hertzienne,
Universite de Lille-Flandres-Artois, CNRS,
59655 Villeneuve d'Ascq, France.

- MA3. HIGH RESOLUTION MICROWAVE FOURIER TRANSFORM AND STARK
EFFECT STUDIES OF SMALL NITROGEN COMPOUNDS.....35 min.

DIETER H. SUTTER, Christian-Albrechts-Universitat, Kiel,
Germany.

Intermission

COBLENTZ PRIZE AND AWARD LECTURE (11 A.M. - 12 NOON)

- MA4. CHEMISTRY AND SPECTROSCOPY AT MATERIALS INTERFACES:WHAT WE KNOW
AND KNOW NOT.....35 min.

P. W. BOHN, Department of Chemistry and Beckman Institute,
University of Illinois at Urbana-Champaign, Urbana, Illinois,
61801.

MEMO TO THOSE CHAIRING SESSIONS

The program as given in this BOOK OF ABSTRACTS incorporates all changes that came to our attention until May 1. Please follow the schedules as given in this book while conducting sessions.

YOUR HELP IS APPRECIATED IMMENSELY

MONDAY, JUNE 17, 1991 -- 1:30 P.M.

Room 1153, Physics Laboratory

Chair Before Intermission: **MARK. D. MARSHALL**, Amherst College, Amherst, Massachusetts.

Chair After Intermission: **J. S. MUENTER**, University of Rochester, Rochester, New York.

ME1. THE INFRARED SPECTRUM OF Ar-HCOH REVISITED.....15 min.(1:30)

T. A. HU, LING HONG SUN, and J. S. MUENTER, Department of Chemistry, University of Rochester, Rochester, New York, 14627.

ME2. THE DIPOLE MOMENT OF CO₂-CO.....10 min.(1:47)

RATAN BHATTACHARJEE, MICHAEL SZAFRANSKI, and J. S. MUENTER, Department of Chemistry, University of Rochester, Rochester, New York, 14627.

ME3. DISSOCIATION OF SMALL METHANOL CLUSTERS AFTER EXCITATION OF THE O-H STRETCH VIBRATION AT 2.7 μ15 min.(1:59)

A. KULCKE, F. HUISKEN, Max-Planck-Institut für Strömungsforschung, D-3400 Göttingen, Federal Republic of Germany; C. LAUSH and J. M. LISY, Department of Chemistry, University of Illinois, Urbana, Illinois, 61801.

ME4. SPECTROSCOPY AND RELAXATION OF I₂-Ar_n CLUSTERS: GEMINATE RECOMBINATION WITHIN SMALL GAS PHASE CLUSTERS.....15 min.(2:16)

J. TELLINGHUISEN, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235; S. FEI, X. ZHENG, and M. C. HEAVEN, Department of Chemistry, Emory University, Atlanta, Georgia, 30322.

ME5. SPECTROSCOPY AND PREDISSOCIATION DYNAMICS OF OH/D-Ne A² Σ^+15 min.(2:33)

S. FEI, X. ZHENG, Y. LIN, and M. C. HEAVEN, Department of Chemistry, Emory University, Atlanta, Georgia, 30322.

ME6. MICROWAVE AND INFRARED SPECTRA OF C₂H₄--HCOH.....15 min.(2:50)

G. T. FRASER, F. J. LOVAS, R. D. SUENRAM, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899; J. Z. GILLIES, Department of Chemistry, Siena College, Loudonville, New York, 12221; and C. W. GILLIES, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York, 12180.

Intermission

ME7. OPTHOTHERMAL-DETECTED MICROWAVE-SIDEBAND CO₂-LASER SPECTROSCOPY OF NCH-NH₃.....15 min.(3:20)

G. T. FRASER, A. S. PINE, R. D. SUENRAM, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899; W. A. KREINER, guest researcher at NIST, Permanent address: Abteilung für Physikalische Chemie, Universität Ulm, Oberer Eselsberg, D-7900 Ulm, West Germany.

ME8. MICROWAVE AND SUBMILLIMETER SPECTROSCOPY OF Ar-NH₃ STATES CORRELATING WITH Ar + NH₃ (J=1, |k|=1).....15 min.(3:37)

E. ZWART, H. LINNARTZ, W. LEO MEERTS, Fysisch Laboratorium, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands; G. T. FRASER, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899; D. D. NELSON, JR., Aerodyne Research Corporation, 45 Manning Road, Billerica, Massachusetts, 01821; and W. KLEMPERER, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138.

ME9. MICROWAVE AND TUNABLE FAR-INFRARED LASER SPECTROSCOPY OF AMMONIA-WATER DIMER.....15 min.(3:54)

P. A. STOCKMAN, R.E. BUMGARNER, S. SUZUKI, P. G. GREEN, and G. A. BLAKE, Department of Geology and Planetary Sciences 170-25, California Institute of Technology, Pasadena, California, 91125.

ME10. THE MICROWAVE SPECTRUM OF BENZENE- SO_2 : A NEARLY FREE INTERNAL ROTOR.....15 min.(4:11)

A. TALEB-BENDIAB, K. W. HILLIG, II, and R. L. KUCZKOWSKI, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.

ME11. THE MICROWAVE SPECTRUM OF TOLUENE- SO_2 : A LOW BARRIER INTERNAL ROTOR.....15 min.(4:28)

A. TALEB-BENDIAB, K. W. HILLIG, II, and R. L. KUCZKOWSKI, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.

ME12. VIBRATIONAL AND ROTATIONAL PROPENSITY RULES FOR THE VIBRATIONAL PREDISSOCIATION OF Ar-CO_2Arrived Late.....15 min.(4:45)

E. J. BOHAC, MARK D. MARSHALL, and R. E. MILLER, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, 27599; Permanent address of Marshall: Department of Chemistry, Amherst College, Amherst, Massachusetts, 01002.

ME13. PERTURBATIONS IN THE 3μ VIBRATIONAL SPECTRUM OF THE ACETYLENE-CARBON MONOXIDE VAN DER WAALS MOLECULE, HOCH-COArrived Late.....15 min.(5:02)

MARK D. MARSHALL, R. E. Miller, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, 27599; J. S. MUENTER, Department of Chemistry, University of Rochester, Rochester, New York, 14627; Permanent address of Marshall: Department of Chemistry, Amherst College, Amherst, Massachusetts, 01002.

TO ALL THOSE PRESENTING PAPERS:

Please use 2" x 2" (5 cm x 5 cm) slides and give them to the projectionist at the beginning of the session.

Overhead projectors are available in each of the rooms where the sessions are held. If you plan to use them, please advise your projectionist at the start of the session so he or she can be ready to have equipment moved around as needed.

Thank you.



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MONDAY, JUNE 17, 1991 — 1:30 P.M.

Room 1009, Physics Laboratory

Chair Before Intermission: L. H. COUDERT, Université Pierre et Marie Curie et CNRS, Paris, France.

Chair After Intermission: R. H. SCHWENDEMAN, Michigan State University, East Lansing, Michigan.

MF1. SPECTRUM OF THE ν_{11} BAND OF CYANURIC FLUORIDE.....10 min.(1:30)

P. E. FLEMING and C. W. MATHEWS, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

MF2. THE BENDING STATES ASSOCIATED WITH THE EXCITED STRETCHING STATES
 ν_1 , ν_2 , $2\nu_3$ and $\nu_2 + \nu_3$ of HCN.....15 min.(1:42)

B. P. WINNEWISSE, M. WINNEWISSE, and S. ALBERT, Physikalisch Chemisches Institut, Justus-Liebig-Universität, D-6300 Giessen, Germany.

MF3. ROVIBRATIONAL ANALYSIS OF THE HIGH RESOLUTION FT-IR SPECTRA OF THE C-N STRETCHING BANDS ν_1 AND ν_2 OF ISOCYANOGEN, CNCN.....15 min.(1:59)

F. STROH and M. WINNEWISSE, Physikalisch Chemisches Institut, Justus-Liebig-Universität, D-6300 Giessen, Germany.

MF4. OBSERVATION OF DYNAMIC STARK SPLITTING IN INFRARED-INFRARED DOUBLE RESONANCE IN METHYL FLUORIDE.....15 min.(2:16)

QUAN SONG and R. H. SCHWENDEMAN, Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824.

MF5. FOREIGN GAS EFFECTS ON COLLISIONAL ENERGY TRANSFER IN METHYL FLUORIDE OBSERVED BY FOUR-LEVEL INFRARED-INFRARED DOUBLE RESONANCE.....15 min.(2:33)

QUAN SONG and R. H. SCHWENDEMAN, Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824.

MF6. POLARIZATION EFFECTS IN INFRARED-INFRARED DOUBLE RESONANCE IN METHYL FLUORIDE.....15 min.(2:50)

UHYON SHIN and R. H. SCHWENDEMAN, Department of Chemistry, Michigan State University, East Lansing, Michigan, 48824.

Intermission

MF7. TRANS-BEND (TUNNELING) AND OVERALL ROTATION ENERGY LEVELS FOR $(\text{HF})_2$ AND ISOTOPOMERS.....Arrived Late15 min.(3:20)

V. C. EPA, P. R. BUNKER, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada; and P. C. GOMEZ, Departamento de Estructura Atómico-Molecular y Espectroscopie, Universidad Complutense de Madrid, 28040 Madrid, Spain.

MF8. TORSIONAL SPECTRA OF CH_3CH_3 AND CD_3CD_3 : INTENSITY ANALYSIS.....15 min.(3:37)

N. MOAZZEN-AHMADI, Department of Physics, University of Lethbridge, Lethbridge, Alberta T1K 3M4, Canada; A.R.W. MCKELLAR, J.W.C. JOHNS, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada; and I. OZIER, Department of Physics, University of British Columbia, Vancouver, British Columbia V6T 2A6, Canada.

MF9. ROTATIONAL DEPENDENCE OF THE PSEUDO-ROTATION TUNNELING SPLITTING IN PF_515 min.(3:54)

L. H. COUDERT, Laboratoire de Physique Moléculaire et Atmosphérique, Université Pierre et Marie Curie et CNRS, 75252 Paris Cedex 05, France.

- MF10. ROVIBRATIONAL HAMILTONIAN FOR TRIATOMIC MOLECULE IN RADAU'S COORDINATES.....15 min.(4:11)
L. H. COUDERT, Laboratoire de Physique Moléculaire et Atmosphérique,
 Université Pierre et Marie Curie et CNRS, 75252 Paris Cedex 05, France.
- MF11. VIBRATIONAL SPECTRA, RING-PUCKERING POTENTIAL ENERGY FUNCTION, AND
 CONFORMATION OF 1,3-DISILACYCLOPENT-4-ENE.....10 min.(4:28)
LLOYD F. COLEGROVE and JAAN LAANE, Department of Chemistry, Texas
 A&M University, College Station, Texas 77843.
- MF12. λ -TYPE RESONANCE IN THE ν_5 BENDING MODE REGION OF C_2H_2 AT 14 μm15 min.(4:40)
MARK WEBER, W. E. BLASS, Molecular Spectroscopy Laboratory, Department
 of Physics and Astronomy, The University of Tennessee, Knoxville,
 Tennessee, 37996-1200; W. C. MAGUIRE, and J. J. HILLMANN, Goddard
 Space Flight Center, Code 693, Greenbelt, Maryland, 20771.
- MF13. PERPENDICULAR BANDS OF CYCLOPROPANE IN THE 3.5 μm REGION.....15 min.(4:57)
D. W. MERDES, Applied Research Laboratory, Pennsylvania State University,
 State College, Pennsylvania, 16804; J. PLIVA, Department of Physics,
 Pennsylvania State University, University Park, Pennsylvania, 16802; and
A. S. PINE, Molecular Physics Division, National Institute of Standards
 and Technology, Gaithersburg, Maryland, 20899.

MONDAY, JUNE 17, 1991 -- 1:30 P.M.

Room 1005, Physics Laboratory

Chair Before Intermission: JULANNA GILBERT, University of Denver, Denver, Colorado.

Chair After Intermission: MARILYN E. JACOX, National Institute of Standards and Technology, Gaithersburg, Maryland.

- MG1. MATRIX REACTIONS OF BORON ATOMS WITH OXYGEN MOLECULES. INFRARED SPECTRA OF SEVERAL BORON-OXYGEN SPECIES.....15 min.(1:30)

T. R. BURKHOLDER and L. ANDREWS, Department of Chemistry, University of Virginia, Charlottesville, Virginia, 22901.

- MG2. MATRIX REACTIONS OF SULFUR ATOMS AND FLUORINE. INFRARED SPECTRA OF SF, SF₂ AND SF₃ IN SOLID ARGON.....15 min.(1:47)

P. HASSANZADEH and L. ANDREWS, Department of Chemistry, University of Virginia, Charlottesville, Virginia, 22901.

- MG3. INFRARED SPECTRA OF NEW NITROGEN-SULFUR SPECIES IN ARGON MATRICES.....15 min.(2:04)

P. HASSANZADEH and L. ANDREWS, Department of Chemistry, University of Virginia, Charlottesville, Virginia, 22901.

- MG4. THE VIBRATIONAL SPECTRA OF CO⁺, C₂O₂⁺, AND C₂O₂⁻ ISOLATED IN SOLID NEON.....15 min.(2:21)

WARREN E. THOMPSON, National Science Foundation, Washington, D.C., 20550; and MARILYN E. JACOX, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

- MG5. THE MID-AND NEAR-INFRARED SPECTRA OF HC₂ ISOLATED IN SOLID ARGON AND NEON.....15 min.(2:38)

DANIEL FORNEY and MARILYN E. JACOX, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

Intermission

- MG6. MATRIX ISOLATION STUDIES OF CHEMICAL VAPOR DEPOSITION: THE (CH₃)₃Ga/AsH₃ AND (CH₃)₃Ga/PH₃ SYSTEMS.....15 min.(3:05)

ELIZABETH A. PIOCOS and BRUCE S. AULT, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, 45221-0172.

- MG7. INFRARED MATRIX ISOLATION STUDY OF THE REACTION OF B₂H₆ WITH NH₃ AND THE METHYLAMINES.....15 min.(3:22)

JOHN D. CARPENTER and BRUCE S. AULT, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, 45221-0172.

- MG8. SPECTROSCOPY OF LOW TEMPERATURE MATRIX ISOLATED NX₂ RADICALS.....15 min.(3:39)

JULANNA V. GILBERT, Department of Chemistry, University of Denver, Denver, Colorado, 80208.

- MG9. CHARACTERIZATION OF TRAPPING SITES IN RELAXED RARE GAS MATRICES USING MONTE-CARLO SIMULATIONS OF INFRARED MATRIX SHIFTS.....15 min.(3:56)

MARK R. DAVIES and ROBERT J. LE ROY, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

- MG10. OBSERVATION OF A C≡C STRETCHING FUNDAMENTAL FOR C₆H IN SOLID Ar.....15 min.(4:13)

T. J. DOYLE, W.R.M. GRAHAM, Department of Physics, Texas Christian University, Fort Worth, Texas, 76129; and L. N. SHEN, Chemical Engineering, Yale University, New Haven, Connecticut, 06520.

MG11. FT VIBRATIONAL SPECTROSCOPY OF Si_2C IN SOLID ARGON.....15 min.(4:30)

J. D. PRESILLA-MÁRQUEZ, C.M.L. RITTBY, and W.R.M. GRAHAM, Department
of Physics, Texas Christian University, Forth Worth, Texas 76129.

MG12. DIATOMIC MOLECULES FORMED BY Mo AND W WITH Cu, Ag, AND Au.....Arrived Late.....15 min.(4:47)

Y. M. HAMRICK, R. J. VAN ZEE, and W. WELTNER, JR., Department of
Chemistry, University of Florida, Gainesville, Florida, 32611-2046.

MG13. THE GROUND STATE OF THE B_3 MOLECULE.....Arrived Late.....10 min.(5:04)

Y. M. HAMRICK, R. J. VAN ZEE, and W. WELTNER, JR., Department of
Chemistry, University of Florida, Gainesville, Florida, 32611-2046.

TUESDAY, JUNE 18, 1991 -- 8:30 A.M.

Room 1153, Physics Laboratory

Chair Before Intermission: MAN-CHOR CHAN, University of Chicago, Chicago, Illinois.

Chair After Intermission: V. MALATHY DEVI, College of William and Mary, Williamsburg, Virginia.

- TA1. HIGH SENSITIVE LASER SPECTROSCOPY OF HIGHLY EXCITED MOLECULAR STATES
..... Invited Paper.....30 min.(8:30)

L. N. SINITSA, Institute of Atmospheric Optics, SB USSR Academy of Science, Tomsk, 634055, USSR.

- TA2. INTERFACING A 4 METER BASE LENGTH MULTIPASS CELL WITH THE BRUKER FTIR:
(0,3,1) AND (1,1,1) BANDS OF D₂O.....15 min.(9:02)

P. S. ORMSBY, K. NARAHARI RAO, Department of Physics, The Ohio State University, Columbus, Ohio, 43210; M. WINNEWISSER, and B. P. WINNEWISSER, Physikalisch-Chemisches Institut, Justus-Liebig-Universität, D-6300 Giessen, Germany.

- TA3. IR SPECTROSCOPY WITH A DOUBLE MODULATION SIDEBAND TECHNIQUE.....15 min.(9:18)

W. A. KREINER, L. JÜRISSEN, W. HÖHE, Abteilung Physikalische Chemie, Universität Ulm, D-7900 Ulm, Germany; and M. LOETE, Laboratoire de Spectronomie Moléculaire et Instrumentation Laser, F-21 000 Dijon, France.

- TA4. HIGH RESOLUTION FOURIER TRANSFORM SPECTROSCOPY IN A SUPERSONIC EXPANSION.....15 min.(9:34)

RICHARD DISSLY, R. E. BUMGARNER, G. A. BLAKE, Division of Geological and Planetary Sciences, 170-25 Caltech, Pasadena, California, 91125; and H. M. PICKETT, Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, California, 91109.

- TA5. THE HIGH RESOLUTION EMISSION SPECTRUM OF GASEOUS LiF.....10 min.(9:50)

H. G. HEDDERICH, P. F. BERNATH, Department of Chemistry, Centre for Molecular Beam and Laser Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada; C. I. FRUM, and R. ENGLEMAN, JR., Department of Chemistry, University of Arizona, Tucson, Arizona, 85721.

- TA6. HIGH RESOLUTION INFRARED SPECTROSCOPIC DIAGNOSTICS OF AC GLOW DISCHARGES.....15 min.(10:01)

S. S. LEE, C. M. GABRYS, M. RÜSSELEIN, and T. OKA, Department of Chemistry and Department of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637.

Intermission

- TA7. OBSERVATION OF THE $3\nu_2 + 0$ OVERTONE BAND OF H₃⁺.....15 min.(10:30)

S. S. LEE, T. OKA, Department of Chemistry and Department of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637; B. F. VENTRUDO, D. T. CASSIDY, Department of Engineering Physics, McMaster University, Hamilton, Ontario L8S 4M1, Canada; S. MILLER, and J. TENNYSON, Department of Physics and Astronomy, University College London, London, United Kingdom WC1E 6BT.

- TA8. OBSERVATION OF FORBIDDEN TRANSITIONS OF H₃⁺.....15 min.(10:46)

L.-W. XU, M. RÜSSELEIN, C. GABRYS, and T. OKA, Department of Chemistry and Department of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637.

TA9. INFRARED SPECTROSCOPY AND EQUILIBRIUM STRUCTURE OF H_2O^+15 min.(11:02)

T. R. HUET, T. OKA, Department of Chemistry and Department of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637; C. J. PURSELL, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405; W. C. HO, Department of Physics, University of British Columbia, Vancouver, British Columbia V6T 2A6, Canada; and B. M. DINELLI, Istituto di Spettroscopia Molecolare, Via de'Castagnoli 1; 40126 Bologna, Italy.

TA10. INFRARED STUDIES OF THE ν_4 BAND OF CH_2D^+15 min.(11:18)

M. RÖSSLEIN, M.-F. JAGOD, C. GABRYS, and T. OKA, Department of Chemistry and Department of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637-1403.

TA11. INFRARED SPECTROSCOPIC STUDY OF THE QUASILINEARITY OF NH_2^+ ION.....15 min.(11:34)

Y. KABBADJ, T. R. HUET, T. OKA, Department of Chemistry and Department of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois, 60637; S. E. CHOI, The James Frank Institute, University of Chicago, Chicago, Illinois, 60637.

TA12. NEW OBSERVATIONS OF ELECTRONIC TRANSITIONS OF H_3 AND D_3 IN THE INFRARED AND VISIBLE REGIONS.....Late Paper added to Abstracts Book.....15 min.(11:50)

W. A. MAJ-WSKI, D. SADOVSKII, A.R.W. McKELLAR, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada; and M. VERVLOET, Laboratoire de Photophysique Moleculaire du CNRS, Université de Paris-Sud, 91405 Orsay, France.

TUESDAY, JUNE 18, 1991 -- 8:30 A.M.

Room 1009, Physics Laboratory

Chair: JOYCE GUEST, University of Cincinnati, Cincinnati, Ohio.

TB1. SUB-DOPPLER INTRACAVITY LASER SPECTROSCOPY OF CoO AND VO.....15 min.(8:30)

G. HUANG, A. J. MERER, Department of Chemistry, University of British Columbia, Vancouver, British Columbia V6T 1Y6, Canada; D. J. CLOUTHIER, Department of Chemistry, University of Kentucky, Lexington, Kentucky, 40506-0055.

TB2. A NEW $^5\Pi$ ELECTRONIC STATE OF PtO.....10 min.(8:47)

C. I. FRUM, R. ENGLEMAN, JR., and P. F. BERNATH, Department of Chemistry, University of Arizona, Tucson, Arizona, 85721.

TB3. HIGH RESOLUTION FOURIER TRANSFORM INFRARED SPECTROSCOPY OF THE $A^2\Pi_1 - X^2\Sigma$ TRANSITION OF CP.....10 min.(8:59)

R. S. RAM, S. TAM, Department of Chemistry, University of Arizona, Tucson, Arizona, 85721; and P. F. BERNATH, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

TB4. LASER SPECTROSCOPY OF STRONTIUM MONOXIDE NEAR 16800 cm^{-1} : ABSORPTION FROM THE LOW LYING $^1\Pi$ AND $^3\Pi$ STATES.....10 min.(9:11)

R.F.W. HERRMANN and W. E. ERNST, Department of Physics, Pennsylvania State University, University Park, Pennsylvania, 16802.

TB5. ANALYSIS OF THE 6100 , 6900 , AND 10200 cm^{-1} RYDBERG-RYDBERG TRANSITIONS OF ArD.....15 min.(9:23)

I. DABROWSKI, G. HERZBERG, J.W.C. JOHNS, D. SADOVSKII, and M. VERVOLET, Herzberg Institute of Astrophysics, National Research Council, Ottawa, Ontario K1A 0R6, Canada.

TB6. HIGH RESOLUTION INFRARED FOURIER TRANSFORM EMISSION SPECTRUM OF THE N_2^+ MEINEL SYSTEM $A^2\Pi_u - X^2\Sigma_g^+$15 min.(9:40)

D. W. FERGUSON, K. NARAHARI RAO, Department of Physics, The Ohio State University, Columbus, Ohio, 43210; G. GUELACHVILI, and P. A. MARTIN, Laboratoire d'Infrarouge, Université de Paris-Sud, 91405 Orsay Cedex, France.

Intermission

TB7. EUV ABSORPTION SPECTROSCOPY OF SUPERSONIC-JET-COOLED MOLECULES: N_2 BANDS IN THE WAVELENGTH REGION $95\text{--}100\text{ nm}$10 min.(10:10)

K. YOSHINO, PETER L. SMITH, W. H. PARKINSON, Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts, 02138; K. P. HUBER, Herzberg Institute of Astrophysics, NRC, Ottawa, Ontario K1A 0R6, Canada; G. STARK, Department of Physics, Wellesley College, Wellesley, Massachusetts, 02181; and K. ITO, Photon Factory, KEK, Tsukuba, Ibaraki 305, Japan.

TB8. FOURIER TRANSFORM SPECTROSCOPY IN THE VUV REGION, THE ABSORPTION BANDS OF NO.....10 min.(10:22)

K. YOSHINO, J. R. ESMOND, W. H. PARKINSON, Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts, 02138; and A. P. THORNE, Imperial College of Science and Technology, London SW7 2BZ, England.

TB9. THE d-s STABILIZATION ENERGY OF THE RARE EARTH OXIDES AND FLUORIDES [Ba-Lu]....15 min.(10:34)

L. A. KALEDIN, High Temperature Institute of the USSR Academy of Sciences, Moscow, 127412, USSR and visiting scientist at MIT; E. J. HILL, and R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.

TB10. THE LOW-LYING STATES OF THE URANIUM MONOXIDE (UO) MOLECULE.....15 min.(10:59)

L. A. KALÉDIN, High Temperature Institute of the USSR Academy of Sciences, Moscow, 127412, USSR and visiting scientist at MIT, Cambridge, Massachusetts, 02139.

TB11. FOURIER TRANSFORM SPECTROSCOPY OF THE $1^3\Delta_g - b^3\Pi_u$ TRANSITION IN $^6\text{Li}_2$15 min.(11:16)

C. LINTON, Department of Physics, University of New Brunswick, Fredericton, New Brunswick E3B 5A3, Canada; R. BACIS, P. CROZET, F. MARTIN, A. J. ROSS, Laboratoire de Spectrometrie Ionique et Moléculaire, Université Claude Bernard, Lyon I, 69622, Villeurbanne Cedex, France; and J. VERGES, Laboratoire Aimé Cotton, Centre National de la Recherche Scientifique II, Université de Paris-Sud (Paris XI), 91405, Orsay Cedex, France.

TB12. THE FIRST NEGATIVE (B-X) SYSTEM OF $^{13}\text{C}^{18}\text{O}^+$: PRECISE MOLECULAR CONSTANTS OF ITS $X^2\Sigma^+$, $A^2\Pi_1$ AND $B^2\Sigma^+$ STATES.....15 min.(11:33)

C.V.V. PRASAD, Department of Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada; and S. PADDI REDDY, Department of Physics, Memorial University of Newfoundland, St. John's, Newfoundland A1B 3X7, Canada.

TB13. THE ELECTRIC DIPOLE MOMENT OF DYSPROSIUM MONOXIDE(DyO)
.....Late Paper Added to Abstracts Book.....15 min.(11:50)

C. LINTON, Department of Physics, University of New Brunswick, Fredericton, New Brunswick E3B 5A3, Canada; and B. SIMARD, Laser Chemistry Group, Steacie Institute for Molecular Sciences, National Research Council, Ottawa, Ontario K1A 0R6, Canada.

TUESDAY, JUNE 18, 1991 -- 8:30 A.M.

Room 1005, Physics Laboratory

Chair: JIM COE, The Ohio State University, Columbus, Ohio.

TC1. VIBRATIONAL SPECTROSCOPY OF TRANS-3,4-DIFLUOROCYCLOBUTENE.....10 min.(8:30)

NORMAN C. CRAIG, SUSAN E. HAWLEY, and ANN PEARSON, Department of Chemistry, Oberlin College, Oberlin, Ohio, 44074.

TC2. FAR-INFRARED SPECTRA AND TWO-DIMENSIONAL POTENTIAL ENERGY SURFACE FOR THE RING-TWISTING AND RING-BENDING VIBRATIONS OF CYCLOHEXENE AND ITS DEUTERATED DERIVATIVES.....15 min.(8:41)

S. J. LEIBOWITZ, J. LAANE, Department of Chemistry, Texas A&M University, College Station, Texas 77843; and V. E. RIVERA-GAINES, Bristol-Meyers, USBNG, Evansville, Indiana, 47721.

TC3. FAR-INFRARED SPECTRA AND TWO-DIMENSIONAL RING-BENDING POTENTIAL ENERGY SURFACE OF 1,3-OXATHIOLANE.....10 min.(8:57)

S. J. LEIBOWITZ, J. LAANE, Department of Chemistry, Texas A&M University, College Station, Texas, 77843; and J. R. VILLARREAL, Pan American University, Edinburg, Texas, 78539.

TC4. REINVESTIGATION OF THE FAR-INFRARED SPECTRA OF THE OUT-OF-PLANE VIBRATIONS OF 1,3-DIOXOLANE.....10 min.(9:08)

E. CORTEZ and J. LAANE, Department of Chemistry, Texas A&M University, College Station, Texas, 77843.

TC5. ANALYSIS OF THE TRANSITION FROM NORMAL MODES TO LOCAL MODES.....15 min.(9:19)

S. ABBATE, G. LONGHI, Dipartimento di Chimica Fisica, Università di Palermo, via Archirafi 26, 90123 Palermo, Italy; C. ZAGANO, G. BOTTO, D. GHISLETTI, Dipartimento di Fisica, Università de Milano, via Celoria 16, 20133 Milano, Italy; AND L. LESPADE, Laboratoire de Spectroscopie Moléculaire et Cristalline, Université de Bordeaux I, 351 Crs. de la Libération, 33405 Talence, France.

TC6. CONFORMATIONAL STABILITY, BARRIERS TO INTERNAL ROTATION, VIBRATIONAL ASSIGNMENT, AND AB INITIO CALCULATIONS OF TRANS-1,3-DICHLOROPROPENE.....15 min.(9:35)

T. G. COSTNER, T. S. LITTLE, J. R. DURIG, Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208; and D. T. DURIG, Departments of Chemistry and Physics, University of the South, Sevanee, Tennessee, 37375.

Intermission

TC7. PERTURBATIVE TREATMENTS OF HIGHLY EXCITED ROTATION-VIBRATION STATES USING CURVILINEAR COORDINATES.....15 min.(10:05)

DARIN C. BURLEIGH, ANNE B. MCCOY, and EDWIN L. SIBERT, III, Department of Chemistry and Theoretical Chemistry Institute, University of Wisconsin-Madison, Madison, Wisconsin, 53706.

TC8. INVESTIGATING THE SEPARABILITY OF VIBRATIONAL MOTIONS.....15 min.(10:21)

RUDOLPH C. MAYRHOFER and EDWIN L. SIBERT, III, Department of Chemistry and Theoretical Chemistry Institute, University of Wisconsin-Madison, Madison, Wisconsin, 53706.

TC9. CALCULATION OF IR INTENSITIES OF HIGHLY EXCITED VIBRATIONAL STATES IN HCN USING VAN VLECK PERTURBATION THEORY.....15 min.(10:37)

ANNE B. MCCOY and EDWIN L. SIBERT, III, Department of Chemistry and Theoretical Chemistry Institute, University of Wisconsin-Madison, Madison, Wisconsin, 53706.

- TC10. REDUCED MASS OF RING PUCKERING AS A FUNCTION OF PUCKERING COORDINATES FOR RING MOLECULES.....10 min.(10:53)
WENYUN ZHAO and J. R. DURIG, Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.
- TC11. SF₆ GAS INTEGRATED INTENSITIES AS A FUNCTION OF DENSITY.....15 min.(11:04)
CORINNE T. DELAYE and MICHAEL E. THOMAS, Applied Physics Laboratory, The Johns Hopkins University, Laurel, Maryland, 20723.
- TC12. CONTINUUM ABSORPTION MEASUREMENTS AND LINE SHAPE MODEL COMPARISONS.....15 min.(11:20)
MICHAEL E. THOMAS and CORINNE T. DELAYE, Applied Physics Laboratory, The Johns Hopkins University, Laurel, Maryland, 20723.
- TC13. PIEZOELECTRIC DETECTION OF OVERTONE SPECTRA OF LIQUIDS WITH C.W. LASER EXCITATION.....15 min.(11:36)
CARLOS MANZANARES and VICTOR BLUNT, Department of Chemistry, Baylor University, Waco, Texas, 46498.
- TC14. INFRARED AND RAMAN SPECTRA AND VIBRATIONAL ANALYSES OF CYCLOPENTADIENYL THALLIUM.....Late Paper Added to Abstracts Book.....10 min.(11:52) CANCELLED
V. A. MEIER, New Jersey Medical College, Newark, New Jersey; and D. P. MCDERMOTT, Division of Science and Math, Lees College, Jackson, Kentucky, 41339.

TUESDAY, JUNE 18, 1991 -- 1:30 P.M.

Room 1153, Physics Laboratory

Chair: R. E. BUMGARNER, California Institute of Technology, Pasadena, California.

- TE1. THE ROTATIONALLY RESOLVED, NEAR INFRARED SPECTRUM OF THE ARGON-METHYLACETYLENE VAN DER WAALS COMPLEX.....15 min.(1:30)

THOMAS A. BLAKE, SHAO-HUI TSENG, MARIUS LEWERENZ, PAUL SWIFT, and ROBERT O. WATTS, Department of Chemistry BG-10, University of Washington, Seattle, Washington, 98195.

- TE2. CORIOLIS COUPLING IN THE LOWEST Π STATE OF Ar-HBr AND Ar-HCl.....15 min.(1:47)

S. W. REEVE, M. A. DVORAK, K. R. LEOPOLD, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, 55455; and D. W. FIRTH, Tennessee Eastman Corporation, Kingsport, Tennessee, 37662.

- TE3. POTENTIAL ANISOTROPY AND THE INFRARED SPECTRA OF H_2 -CO AND H_2 -N₂ VAN DER WAALS COMPLEXES.....15 min.(2:04)

CLAUDIO CHUAQUI and ROBERT J. LE ROY, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

- TE4. AN "ITERATIVE SECULAR EQUATION" METHOD FOR CALCULATING ROVIBRATIONAL STATES OF WEAKLY-BOUND COMPLEXES.....15 min.(2:21)

TOM SLEE and ROBERT J. LE ROY, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

- TE5. DEVELOPMENT OF A FULL 3-DIMENSIONAL POTENTIAL ENERGY SURFACE FOR He-HF FROM HIGH-RESOLUTION SPECTROSCOPY.....15 min.(2:38)

TOM SLEE and ROBERT J. LE ROY, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

- TE6. SPECTROSCOPIC DIAGNOSTICS FOR TEMPERATURE, CLUSTER SIZE AND DEGREE OF SOLVATION IN INHOMOGENEOUS VAN DER WAALS CLUSTERS.....15 min.(2:55)

MARY ANN KMETIC and ROBERT J. LE ROY, Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

Intermission

- TE7. TUNNELING SPLITTINGS IN A-BX₄ TYPE VAN DER WAALS MOLECULES.....15 min.(3:27)

NOBUKIMI OHASHI, Department of Physics, Faculty of Science, Kanazawa University, Kanazawa 920, Japan; and JON T. HOUGEN, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

- TE8. MICROWAVE SPECTRUM AND STRUCTURE OF THE KETENE-ETHYLENE COMPLEX: AN EXAMPLE OF THE $2\pi + 2\pi$ CYCLOADDITION REACTION.....15 min.(3:44)

F. J. LOVAS, R. D. SUENRAM, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899; C. W. GILLIES, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York, 12180; and J. Z. GILLIES, Department of Chemistry, Siena College, Loudonville, New York, 12221.

- TE9. MICROWAVE SPECTRUM AND STRUCTURE OF THE OC-SO₂ COMPLEX.....10 min.(4:01)

F. J. LOVAS and R. D. SUENRAM, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

- TE10. ROTATIONAL SPECTRUM OF THE METHANE-WATER VAN DER WAALS COMPLEX.....15 min.(4:13)
R. D. SUENRAM, G. T. FRASER, and F. J. LOVAS, Molecular Physics
 Division, National Institute of Standards and Technology, Gaithersburg,
 Maryland. 20899.
- TE11. DEUTERATED-ACETYLENE DIMERS: THE TUNNELING MOTIONS OF (DCCD)₂, (DCCH)₂,
 DCCD-DCCH, DCCH-DCCD, HCCH-DCCD, AND HCCH-DCCH FROM THEIR
 MICROWAVE SPECTRA.....15 min.(4:30)
 K. MATSUMURA, Seinan Gakuin University, Nishijin, Sawaraku, Fukuoka 814,
 Japan; F. J. LOVAS, R. D. SUENRAM, Molecular Physics Division, National
 Institute of Standards and Technology, Gaithersburg, Maryland, 20899.
- TE12. DISSOCIATION OF B STATE I₂ INDUCED IN VAN DER WAALS COMPLEXES...Arrived Late...15 min.(4:47)
M. L. BURKE and W. KLEMPERER, Department of Chemistry, Harvard
 University, Cambridge, Massachusetts, 02138.
- TE13. STRUCTURE AND INTERNAL MOTION OF COMPLEXES OF NCCN WITH NCCN,
 NH₃ AND H₂O.....Arrived Late.....15 min.(5:04)
I. SUNI, S. LEE, and W. KLEMPERER, Department of Chemistry,
 Harvard University, Cambridge, Massachusetts, 02138.

TUESDAY, JUNE 138, 1991 — 1:30 P.M.

Room 1009, Physics Laboratory

Chair: ARLAN MANTZ, Franklin and Marshall College, Lancaster, Pennsylvania.

TF1. PURE ROTATIONAL TRANSITIONS IN SOLID PARA HYDROGEN.....15 min.(1:30)

T. BYERS and T. OKA, Department of Chemistry and Department of
Astronomy and Astrophysics, University of Chicago, Chicago, Illinois,
60637-1403.

TF2. CRYSTAL FIELD SPLITTING OF THE $\Delta J=6$ PURE ROTATIONAL $W_0(0)$ TRANSITION
OF SOLID HYDROGEN: THEORY AND OBSERVATION.....15 min.(1:47)

MAN-CHOR CHAN and TAKESHI OKA, Department of Chemistry and Department
of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois,
60637-1403.

TF3. ANALYSIS OF THE NEAREST NEIGHBORING (nn)o-H₂ PAIR TRANSITIONS IN THE
FUNDAMENTAL Q-BRANCH OF SOLID HYDROGEN: GROUP THEORY AND
INTENSITY CALCULATIONS.....15 min.(2:04)

MAN-CHOR CHAN and TAKESHI OKA, Department of Chemistry and Department
of Astronomy and Astrophysics, University of Chicago, Chicago, Illinois,
60637-1403.

TF4. DYE LASER SPECTROSCOPY OF MOLECULAR HYDROGEN.....15 min.(2:21)

DAVID FERGUSON, K. NARAHARI RAO, Department of Physics, The Ohio State
University, Columbus, Ohio, 43210; LEE LARSEN, and M. E. MICKELSON,
Department of Physics and Astronomy, Denison University, Granville,
Ohio, 43023.

TF5. INDUCED INFRARED ABSORPTION SPECTRA OF THE DOUBLE TRANSITIONS $H_2(v=0+1)$
+ $D_2(v=0+1)$15 min.(2:38)

C.T.W. HSIEH and S. PADDI REDDY, Department of Physics, Memorial
University of Newfoundland, St. John's, Newfoundland A1B 3X7, Canada.

TUESDAY, JUNE 18, 1991 -- 3:05 P.M.

Room 1009, Physics Laboratory

Chair: ARLAN MANTZ, Franklin and Marshall College, Lancaster, Pennsylvania.

TF'1. ANALYSIS OF THE 5_0^1 , 6_0^1 , 8_0^1 AND 9_0^1 BANDS OF CH_2DF10 min.(3:05)

W. LEWIS-BEVAN, W. D. STORK, Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois, 62901-4409;
D. F. EGGERS, Department of Chemistry BG-10, University of Washington, Seattle, Washington, 98195; and M.C.L. GERRY, Department of Chemistry, University of British Columbia, Vancouver, British Columbia V6T 1Y6, Canada.

TF'2. INFRARED DIODE LASER SPECTROSCOPY OF FORMYL CHLORIDE: THE ν_6 BAND.....10 min.(3:17)

DON E. KRISTIANSEN and W. LEWIS-BEVAN, Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois, 62901-4409.

TF'3. ANALYSIS OF THE CORIOLIS COUPLED 4_0^1 AND 6_0^1 BANDS OF DBF_210 min.(3:29)

W. D. STORK and W. LEWIS-BEVAN, Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois, 62901-4409.

TF'4. AB INITIO CALCULATION OF VIBRATIONAL ABSORPTION AND CIRCULAR DICHROISM SPECTRA USING MP2 FORCE FIELDS: ASSIGNMENT OF THE VIBRATIONAL SPECTRA OF 2-OXETANONE, 4-METHYL AND 3-METHYL-2-OXETANONE.....15 min.(3:41)

C. CHABALOWSKI, U. S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, Maryland, 21005-5066; K. J. JALKANEN, F. J. DEVLIN, and P. J. STEPHENS, Department of Chemistry, University of Southern California, Los Angeles, California, 90089-0482.

TF'5. AB INITIO CALCULATION OF VIBRATIONAL ABSORPTION AND CIRCULAR DICHROISM SPECTRA USING MP2 FORCE FIELDS: CONFORMATIONAL ANALYSIS OF METHYL GLYCOLATE AND METHYL LACTATE.....15 min.(3:58)

R. BURSI, F. J. DEVLIN, P. J. STEPHENS, Department of Chemistry, University of Southern California, Los Angeles, California, 90089-0482; and C. CHABALOWSKI, U. S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, Maryland, 21005-5066.

TF'6. FORMALISM FOR THE CALCULATION OF ATOMIC POLAR AND AXIAL TENSORS USING LOCALIZED MOLECULAR ORBITALS.....15 min.(4:15)

T. D. BOUMAN, Department of Chemistry, Southern Illinois University, Edwardsville, Illinois, 62026; A. E. HANSEN, Department of Physical Chemistry, H. C. Ørsted Institute, DK-2100 Copenhagen Ø, Denmark; and P. J. STEPHENS, Department of Chemistry, University of Southern California, Los Angeles, California, 90089-0482.

TF'7. MODELLING THE POTENTIAL ENERGY HYPERSURFACE OF THE HYDROGEN BOND $\text{HCN}\cdots\text{HF}$Arrived Late.....15 min.(4:32)

A. QUINONES, G. BANDARAGE, R. R. LUCCHESI, and J. W. BEVAN, Department of Chemistry, Texas A&M University, College Station, Texas, 77843.

TF'8. INVESTIGATION OF RELATIVISTIC EFFECTS IN HYDROGEN BOND INTERACTIONS: $\text{OC}\cdots\text{HI}$Arrived Late.....15 min.(4:49)

A. SUCKLEY, A. C. LFGON, Christopher Ingold Laboratories, Chemistry Department, University College, London, London WC1 HOAJ, United Kingdom; Z. WANG, G. BANDARAGE, R. R. LUCCHESI, and J. W. BEVAN, Department of Chemistry, Texas A&M University, College Station, Texas, 77843.

TUESDAY, JUNE 18, 1991 — 1:30 P.M.

Room 1005, Physics Laboratory

Chair: JANE RICE, Naval Research Laboratory, Washington, D.C.

- TG1. RADIATIVE TRANSITION PROBABILITIES FOR ALL VIBRATIONAL LEVELS IN THE $X^1\Sigma^+$ STATE OF HF.....15 min.(1:30)

WARREN T. ZEMKE, Department of Chemistry, Wartburg College, Waverly, Iowa, 50677; WILLIAM C. STWALLEY, Center for Laser Science and Engineering, and Departments of Chemistry and Physics, University of Iowa, Iowa City, Iowa, 52242; STEPHEN R. LANGHOFF, Ames Research Center, NASA, Moffett Field, California, 94035; G. L. VALDERAMA, and MICHAEL T. BERRY, Laser Applications Research Center, Houston Area Research Center, 4802 Research Forest Drive, The Woodlands, Texas, 77381 and Rice University, Houston, Texas, 77251.

- TG2. THE MANY-LINE SPECTRA OF OH AND OD NEAR 1850 Å.....15 min.(1:47)

J. A. COXON, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada; F. HOLLAND, Forschungszentrum Jülich GmbH, Institut für Atmosphärische Chemie, D-5170 Jülich, Germany; and K. P. HUBER, Herzberg Institute of Astrophysics, National Research Council, Ottawa, Ontario K1A 0R6, Canada.

- TG3. J-DEPENDENT LIFETIMES OF $\text{NO}(B^2\Pi)_{v=7}$15 min.(2:04)

G. E. GADD, CSIRO Division of Applied Physics, Linfield NSW 2070, Australia; D. L. HUESTIS, and T. G. SLANGER, Molecular Physics Laboratory, SRI International, Menlo Park, California, 94025.

- TG4. HYPERFINE STRUCTURE MEASUREMENTS IN THE $A^3\Pi(1) \leftarrow X^1\Sigma^+$ ELECTRONIC TRANSITION OF I^{13}CI NEAR THE DISSOCIATION LIMIT.....15 min.(2:21)

T. J. SLOTTBACK, K. C. JANDA, D. W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260; J. R. JOHNSON, Thompson Electronics, Dallas, Texas; and C. M. WESTERN, Department of Chemistry, University of Bristol, United Kingdom.

- TG5. OBSERVATION AND ANALYSIS OF ION-PAIR TRANSITIONS OF I_2 IN A FREE-JET EXPANSION.....15 min.(2:38)

J. TELLINGHUISEN, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235; X. ZHENG, S. FEI, and M. C. HEAVEN, Department of Chemistry, Emory University, Atlanta, Georgia, 30322.

- TG6. LASER INDUCED FLUORESCENCE SPECTRUM OF $\text{BiF}(A-X)$15 min.(2:55)

MATTHEW BOHN, CHRIS BERST, and ERNEST A. DORKO, PL/ARDJ, Phillips Laboratory, Kirtland AF Base, New Mexico, 87117-6008.

Intermission

- TG7. HIGH RESOLUTION FOURIER TRANSFORM SPECTROSCOPY OF SUPERSONICALLY COOLED CN RADICAL.....15 min.(3:25)

BRENT D. REHFUSS, M. H. SUH, TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210; and V. E. BONDYBEY, Institut für Physikalische Chemie der Technischen Universität, München, 8046 Garching, Germany.

- TG8. MICROWAVE SPECTROSCOPY OF THE $v=3-10$ LEVELS OF $\text{CN}(X^2\Sigma^+)$15 min.(3:42)

H. ITO, K. KUCHITSU, Department of Chemistry, Nagaoka University of Technology, Nagaoka 940-21, Japan; S. YAMAMOTO, S. SAITO, Department of Astrophysics, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464, Japan.

- TG9. PHOTOFRAGMENT SPECTROSCOPY OF CS_2 AT 206-200 nm.....15 min.(3:59)

CAROLINE STARRS and JOHN HEPBURN, Centre for Molecular Beams and Laser Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

TG10. HIGH RESOLUTION SPECTROSCOPY OF Na_3 BY CW RESONANT TWO-PHOTON IONIZATION.....10 min.(4:16)

STEFAN RAKOWSKY and WOLFGANG E. ERNST, Department of Physics, The Pennsylvania State University, University Park, Pennsylvania, 16802.

TG11. ROTATIONAL, FINE, AND HYPERFINE STRUCTURE OF Ar-OH VAN DER WAALS COMPLEX.....15 min.(4:28)

BOR-CHEN CHANG, DAVID W. CULLIN, JAMES M. WILLIAMSON, LIAN YU, BRENT D. REHFUSS, and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

TG12. FLUORESCENCE EXCITATION AND RESOLVED EMISSION SPECTRA OF SUPERSONICALLY COOLED Al_2O10 min.(4:45)

MING-FANG CAI, CHRISTOPHER C. CARTER, TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210; and VLADAMIR E. BONDYBEY, Institut für Physikalische Chemie der Technischen Universität, München, 8046 Garching, Germany.

TG13. LASER INDUCED FLUORESCENCE AND STIMULATED EMISSION PUMPING OF CD_215 min.(4:57)

WEI XIE and HAI-LUNG DAI, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, 19104-6323.

WEDNESDAY, JUNE 19, 1991 -- 8:45 A.M.

Auditorium, Independence Hall

Chair: JON T. HOUGEN, National Institute of Standards and
Technology, Gaithersburg, Maryland

Plenary Session

WA1. SPECTROSCOPY: THE INTERSTELLAR CONNECTION.....35 min.

ERIC HERBST, Department of Physics, Duke University, Durham,
North Carolina, 27706.

WA2. MODELING VIBRATION-ROTATION IN SPHERICAL TOP MOLECULES:
THEORY AND PRACTICE.....35 min.

J. P. CHAMPION, Laboratoire de Spectronomie Moléculaire et
Instrumentation Laser, Université de Bourgogne, Dijon, France.

Intermission

WA3. THEORETICAL ANALYSIS OF ROVIBRATIONAL STRUCTURE. QUANTUM
BIFURCATIONS AND CATASTROPHES.....35 min.

B. I. ZHILINSKII, Department of Chemistry, Moscow State
University, Moscow, USSR.

WA4. SPECTROSCOPY BY AB INITIO QUANTUM CHEMISTRY.....35 min.

NICHOLAS HANDY, Department of Chemistry, University of
Cambridge, Cambridge CB2 1EW, England.

WA5. TENTATIVE IDENTIFICATION OF $(H_2)_2$ DIMER EMISSION IN THE
2-MICRON AURORAL SPECTRUM OF JUPITER
.....Late Paper Added to Abstracts Book.....15 min.

L. M. TRAFTON, McDonald Observatory and Department of Astronomy,
University of Texas at Austin, Austin, Texas, 78712; and
J.K.G. WATSON, Herzberg Institute of Astrophysics, National
Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.

PLEASE NOTE

MOST OF THE CONTRIBUTED PAPERS RECEIVED BETWEEN MON. MARCH 1, 1991 AND
FRI. MARCH 8, 1991 HAVE BEEN DISTRIBUTED BETWEEN SESSIONS TF' AND RC.
THE PRELIMINARY PROGRAM WENT TO THE PRINTERS ON MARCH 8, ONE WEEK AFTER
THE DEADLINE. THE CONTRIBUTED PAPERS RECEIVED BETWEEN MARCH 8 AND MAY 1
HAVE BEEN SCHEDULED IN THIS BOOK OF ABSTRACTS AND IDENTIFIED AS SUCH.

WENDESDAY, JUNE 19, 1991 -- 1:30 P.M.

Room 1153, Physics Laboratory
SEMINAR ON C_{60} AND RELATED COMPOUNDS

Chair Before Intermission: H. W. KROTO, University of Sussex, UK.

Chair After Intermission: R. F. CURL, Rice University, Houston, Texas.

WE1. CARBON CAGE RESEARCH AT RICE UNIVERSITY...Invited paper.....30 min.(1:30)

R. F. CURL, Department of Chemistry, Rice University,
Houston, Texas, 77251.

WE2. FROM INTERSTELLAR DUST TO FULLERENES.....Invited paper.....30 min.(2:03)

WOLFGANG KRÄTSCHMER, Max-Planck-Institut für Kernphysik,
D-6900 Heidelberg, Germany.

WE3. $C_{60}M$ AND $C_{80}M$ COMPLEXES; THEORETICAL TREATMENT OF ELECTRONIC
STRUCTURE, IONIZATION POTENTIALS, AND EXCITATION ENERGIES
.....Invited paper.....30 min.(2:36)

RUSSELL M. PITZER, Department of Chemistry, The Ohio State
University, Columbus, Ohio, 43210.

Intermission

WE4. THE DISCOVERY OF C_{60} , THE THIRD FORM OF CARBON, AND ITS
IMPLICATIONS FOR CHEMISTRY ON EARTH AND IN SPACE..Invited paper..30 min.(3:20)

H. W. KROTO, School of Chemistry and Molecular Sciences,
University of Sussex, Brighton, BN1 9QJ, United Kingdom.

WE5. INFRARED EMISSION SPECTROSCOPY OF GAS PHASE C_{60} ...Invited paper...30 min.(3:53)

PETER BERNATH, Department of Chemistry, The University of
Arizona, Tucson, Arizona, 85721.

WE6. OBSERVATION OF THE DOUBLY CHARGED, GAS PHASE ANION OF
BUCKMINSTERFULLERENE, C_{60}^{2-}10 min.(4:26)

P. A. LIMBACH, L. C. SCHWEIKHARD, K. A. COWEN,
M. T. McDERMOTT, A. G. MARSHALL, AND J. V. COE, Department
of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

WE7. FAR INFRARED BENDING MODE FOR C_4 TRAPPED IN Ar.....15 min.(4:38)

P. A. WITHEY, W. R. M. GRAHAM, Department of Physics,
Texas Christian University, Fort Worth, Texas, 76129,
L. N. SHEN, Chemical Engineering, Yale University,
New Haven, Connecticut, 06520.

WE8. IS C_4 BENT?.....10 min.(4:55)

D. W. EWING, Department of Chemistry, John Carroll
University, Cleveland, Ohio, 44118.

WE9. AB INITIO THEORETICAL PREDICTIONS OF THE EQUILIBRIUM GEOMETRIES OF
 C_{60} , C_{70} , $C_{60}H_{60}$ AND $C_{60}F_{60}$...Late paper added to abstracts book.10 min.(5:07)

GUSTAVO E. SCUSERIA, Rice Quantum Institute, Rice University,
Houston, Texas, 77251-1892.

WE10. THE EPR SPECTRUM OF C_{60} ANION AND CATION RADICALS
.....Late paper added to abstracts book.....10 min.(5:19)

S. G. KUKOLICH, Department of Chemistry, University of Arizona,
Tucson, Arizona, 85721; and D. R. HUFFMAN, Department of Physics,
University of Arizona, Tucson, Arizona, 85721.

WEDNESDAY, JUNE 19, 1991 -- 1:30 P.M.

Room 1009, Physics Laboratory

Chair: L. S. ROTHMAN, Department of the Air Force Geophysics Laboratory(AFSC),
Hanscom Air Force Base, Massachusetts.

WF1. COLLISIONAL LINE MIXING IN THE R_{Q_0} BRANCH OF THE ν_5 BAND OF CH_3Cl15 min.(1:30)

N. LACOME, Laboratoire de Spectrochimie Moléculaire, Université
Pierre et Marie Curie, 75252 Paris Cedex 05, France; L. R. BROWN,
Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, California,
91109; C. CHACKERIAN, JR., NASA Ames Research Center, Moffett Field,
California, 94035-1000; and G. TARRAGO, Laboratoire d'Infrarouge,
CNRS, Associé au Université de Paris sud, 91405 Orsay Cedex, France.

WF2. SELF-BROADENING AND LINE-MIXING IN HCN Q BRANCHES.....15 min.(1:47)

A. S. PINE, Molecular Physics Division, National Institute of Standards
and Technology, Gaithersburg, Maryland, 20899; and J. P. LOONEY,
Thermophysics Division, National Institute of Standards and Technology,
Gaithersburg, Maryland, 20899.

WF3. MEASUREMENTS OF COLLISIONAL WIDTHS OF H_2O FROM FOURIER TRANSFORM FLAME
SPECTRA BETWEEN 800 AND 1800 CM^{-1}10 min.(2:04)

V. DANA, J.-Y. MANDIN, C. CAMY-PEYRET, J.-M. FLAUD, Laboratoire de
Physique Moléculaire et Applications, CNRS et Université Pierre et
Marie Curie, 75252 Paris Cedex 05, France; and L. S. ROTHMAN,
Department of the Air Force Geophysics Laboratory(AFSC), Optical
Physics Division, Hanscom Air Force Base, Massachusetts, 01731-5000.

WF4. N_2 -BROADENING AND LINE SHIFTS IN THE ν_3 BAND OF CO_2 AND THE ν_2 BAND OF H_2O15 min.(2:16)

V. MALATHY DEVI, D. CHRIS BENNER, Department of Physics, College of
William and Mary, Williamsburg, Virginia, 23185; MARY ANN H. SMITH,
and CURTIS P. RINSLAND, Atmospheric Sciences Division, NASA Langley
Research Center, Mail Stop 401A, Hampton, Virginia, 23665-5225.

WF5. LORENTZ BROADENING AND PRESSURE-INDUCED LINESHIFT COEFFICIENTS IN THE ν_2
BAND OF $HD^{16}O$10 min.(2:33)

C. P. RINSLAND, M.A.H. SMITH, Atmospheric Sciences Division, NASA
Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665-5225;
V. MALATHY DEVI, and D. C. BENNER, Department of Physics, College of
William and Mary, Williamsburg, Virginia, 23185.

WF6. NEW CALCULATIONS FOR WATER BY THE TECHNIQUE OF DIRECT NUMERICAL
DIAGONALIZATION.....15 min.(2:45)

RICHARD B. WATTSON and GARY E. GALICA, Visidyne, Inc., 10 Corporate Pl.,
S. Bedford St., Burlington, Massachusetts, 01803.

Intermission

WF7. MEASUREMENTS OF SELF-BROADENING OF OZONE ABSORPTION LINES.....10 min.(3:15)

M.A.H. SMITH, C. P. RINSLAND, Atmospheric Sciences Division, NASA
Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665-5225;
and V. MALATHY DEVI, Department of Physics, College of William and
Mary, Williamsburg, Virginia, 23185.

WF8. TEMPERATURE DEPENDENCE OF N_2 -BROADENING COEFFICIENTS IN THE ν_3 BAND OF OZONE...15 min.(3:27)

M. N. SPENCEP and C. CHACKERIAN, JR., NASA Ames Research Center,
MS 245-4, Moffett Field, California, 94035-1000.

- WF9. THE TEMPERATURE DEPENDENCE OF THE INFRARED ABSORPTION OF N_2O_5 IN THE REGION 300-400 CM^{-1}15 min.(3:44)
- B. P. WINNEWISSER, M. WINNEWISSER, G. SEIBERT, Physikalisch-Chemisches Institut, Justus-Liebig-Universität, D-6300 Giessen, Germany; F. C. DE LUCIA, Department of Physics, The Ohio State University, Columbus, Ohio, 43210; P. HELMINGER, Department of Physics, University of South Alabama, Mobile, Alabama, 36688; and G. PAWELKE, Anorganische Chemie, FB9, Universität, 5600 Wuppertal 1, Germany.
- WF10. OXYGEN-INDUCED BROADENING AND LINE SHIFTS IN THE ν_3 REGION OF $^{12}CH_4$15 min.(4:01)
- D. CHRIS BENNER, V. MALATHY DEVI, Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185; MARY ANN H. SMITH, and CURTIS P. RINSLAND, Atmospheric Sciences Division, NASA Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665-5225.
- WF11. BROADENING AND SHIFTS OF CH_4 LINES IN THE ν_4 BAND AT LOW TEMPERATURES.....15 min.(4:18)
- M.A.H. SMITH, C. P. RINSLAND, Atmospheric Sciences Division, Mail Stop 401A, NASA Langley Research Center, Hampton, Virginia, 23665-5225; V. MALATHY DEVI, and D. C. BENNER, Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185.
- WF12. DIODE LASER MEASUREMENTS OF CO_2 LINE INTENSITIES AT HIGH TEMPERATURE IN THE 4.3 μm REGION.....10 min.(4:35)
- L. ROSENMANN, S. LANGLOIS, J. TAINE, Laboratoire E.M.2.C. du CNRS (UPR 288) et de l'ECP, Ecole Centrale Paris, Grande Voie des Vignes, 92295 Chatenay-Malabry Cedex, France; and C. DELAYE, Applied Physics Laboratory, The Johns Hopkins University, Laurel, Maryland, 20723.
- WF13. PRESSURE BROADENING MEASUREMENTS OF CH_4 AT 77°K BY H_2 AND He...Arrived Late....10 min.(4:47)
- DANIELE ROMANINI and KEVIN K. LEHMANN, Department of Chemistry, Princeton University, Princeton, New Jersey, 08544.
- WF14. FIRST OBSERVATION OF LINES CORRESPONDING TO THE $(03^1_0, 11^1_0)_{II}$ TO 00^0_1 VIBRATIONAL TRANSITION IN NITROUS OXIDE.....
.....Late Paper Added to Abstracts Book.....10 min.(4:59)
- J. M. SIROTA, D. C. REUTER, and M. J. MUMMA, NASA Goddard Space Flight Center, Laboratory for Extraterrestrial Physics, Code 693, Greenbelt, Maryland, 20770.

WEDNESDAY, JUNE 19, 1991 -- 1:30 P.M.

Room 1005, Physics Laboratory

Chair Before Intermission: P. L. POLAVARAPU, Vanderbilt University, Nashville, Tennessee.

Chair After Intermission: T. B. FREEDMAN, Syracuse University, Syracuse, New York.

WG1. INSTRUMENTAL ADVANCES IN THE MEASUREMENT OF RAMAN OPTICAL ACTIVITY.....15 min.(1:30)

D. CHE, G.-S. YU, T. B. FREEDMAN, and L. A. NAFIE, Department of Chemistry, Syracuse University, Syracuse, New York, 13244-4100.

WG2. VIBRATIONAL CIRCULAR DICHROISM AND RAMAN OPTICAL ACTIVITY IN EPHEDRINE MOLECULES.....15 min.(1:47)

N. RAGUNATHAN, T. B. FREEDMAN, D. CHE, and L. A. NAFIE, Department of Chemistry, Syracuse University, Syracuse, New York, 13244-4100.

WG3. METHINE STRETCHING VCD IN HYDROXY ACIDS AND RELATED MOLECULES.....15 min.(2:04)

D. M. GIGANTE, J. E. EVANS, T. B. FREEDMAN, and L. A. NAFIE, Department of Chemistry, Syracuse University, Syracuse, New York, 13244-4100.WG4. VIBRATIONAL CIRCULAR DICHROISM OF (S,S)-OXIRANE-2,3-²H₂ AND (S,S)-CYCLOPROPANE-1,2-²H₂ IN THE GAS PHASE AND SOLUTION.....15 min.(2:21)T. B. FREEDMAN, N. RAGUNATHAN, and L. A. NAFIE, Department of Chemistry, Syracuse University, Syracuse, New York, 13244-4100.

WG5. VIBRATIONAL CIRCULAR DICHROISM STUDY OF [2S,3S]-DIDEUTERIOBUTYRO-LACTONE. COMPARISON OF EXPERIMENTAL AND CALCULATED SPECTRA.....15 min.(2:38)

PETR MALON, LORETTA J. MICKLEY, KATHLEEN SLUIS, TIMOTHY A. KEIDERLING, Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680; JACK UANG, SID KAMATH, and JAMES S. CHICKOS, Department of Chemistry, University of Missouri St. Louis, Missouri, 63121.

WG6. VIBRATIONAL CIRCULAR DICHROISM STUDY OF [3R,4R]-DIDEUTERIOCYCLOBUTANE-1,2-DIONE. COMPARISON OF EXPERIMENT AND CALCULATIONS.....15 min.(2:55)

PETR MALON, KATHLEEN SLUIS, TIMOTHY A. KEIDERLING, Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680; J.-Y. UANG, and JAMES S. CHICKOS, Department of Chemistry, University of Missouri-St. Louis, St. Louis, Missouri, 63121.

Intermission

WG7. EXPERIMENTAL AND AB INITIO THEORETICAL VIBRATIONAL CIRCULAR DICHROISM OF SUBSTITUTED OXIRANES.....15 min.(3:25)

P. L. POLAVARAPU, S. T. PICKARD, H. E. SMITH, and T. M. BLACK, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.

WG8. VIBRATIONAL CIRCULAR DICHROISM OF METHYL AND ETHYL LACTATES.....10 min.(3:42)

P. L. POLAVARAPU, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235; and P. K. BOSE, Department of Chemistry, Government B.M. College, Barisal, Bangladesh.

WG9. NEAR INFRARED CIRCULAR DICHROISM SPECTRA OF (3R)-METHYL CYCLOHEXANONE AND (3R)-METHYL CYCLOPENTANONE.....15 min.(3:54)

S. ABBATE, G. LONGHI, Dipartimento di Chimica Fisica, Università di Palermo, via Archirafi 26, 90123 Palermo, Italy; L. LESPADE, D. CAVAGNAT, Laboratoire de Spectroscopie Moléculaire et Cristalline, Université de Bordeaux I, Crs. de la Liberation 351, 33405 Talence, France; C. BERTUCCI, and P. SALVADORI, Dipartimento di Chimica, Università di Pisa, via Risorgimento 35, 56100 Pisa, Italy.

- WG10. BAND SHAPE OF THE CH_2 STRETCHING BANDS - SOLID POLYETHYLENE...Arrived Late.....15 min.(4:11)
 M. GRANDBOIS, M. TRUDEL, and C. CHAPADOS, Département de Chimie-Biologie, Université du Québec à Trois-Rivières, C.P. 500, Trois-Rivières, Quebec G9A 5H7, Canada.
- WG11. VIBRATIONAL CIRCULAR DICHROISM MEASUREMENTS IN THE FAR INFRARED REGION:
 STATUS REPORT.....Arrived Late.....15 min.(4:28)
P. L. POLAVARAPU, Department of Chemistry, Vanderbilt University, Nashville, Tennessee, 37235.
- WG12. THEORETICAL PREDICTION OF THE MAGNETIC CIRCULAR DICHROISM SPECTRUM IN Cl_2 :
 THE $1^1\Pi_u + X(^1\Sigma_g^+)$ ELECTRONIC TRANSITION.....Arrived Late.....15 min.(4:40)
 GEORGE F. ADAMS and CARY F. CHABALOWSKI, U. S. Army Ballistic Research Laboratory, SLCBR-IB-I, Aberdeen Proving Ground, Maryland, 21005-5066.
- WG13. PHOTOCHEMISTRY OF ACETONE ON NaCl FILMS: AN IR ANALYSIS
Late Paper Added to Abstracts Book.....15 min.(4:57)
HUGH H. RICHARDSON, Department of Chemistry, Ohio University, Athens, Ohio, 45701.

WEDNESDAY, JUNE 19, 1991 -- 1:30 P.M.

Room 1008 Evans Chemical Laboratory

Chair: RODNEY McCORMICK, Department of Physics, The Ohio State University,
Columbus, Ohio.

- WH1. STARK EFFECT IN THE FAR-INFRARED VIBRATION-ROTATION-TUNNELLING SPECTRUM OF
PROPANE-WATER.....Late Paper Added to Abstracts Book.....15 min.(1:30)

DAVID W. STEYERT, MATTHEW J. ELROD, RICHARD J. SAYKALLY, Department of
Chemistry, University of California, Berkeley, California, 94720; and
R. D. SUENRAM, Molecular Physics Division, National Institute of Standards
and Technology, Gaithersburg, Maryland, 20899.

- WH2. TUNABLE FAR INFRARED LASER SPECTROSCOPY OF Ar_nHCl
.....Late Paper Added to Abstracts Book.....15 min.(1:47)

M. J. ELROD, D. W. STEYERT, and R. J. SAYKALLY, Department of Chemistry,
University of California, Berkeley, California, 94720.

- WH3. AlH EINSTEIN EMISSION COEFFICIENTS OF THE $\text{A}^1\Pi - \text{X}^1\Sigma^+$ TRANSITION
.....Late Paper Added to Abstracts Book.....15 min.(2:04)

JANE K. RICE, LOUISE PASTERNAK, and H. H. NELSON, Chemistry Division,
Naval Research Laboratory, Washington, D.C., 20375-5000.

- WH4. THE STRUCTURE AND PHOTOPHYSICS OF BENZENE- $(\text{H}_2\text{O})_1$ AND BENZENE- $(\text{H}_2\text{O})_2$
COMPLEXES.....Late Paper Added to Abstracts Book.....10 min.(2:21)

ALBERT J. GOTCH, AARON W. GARRETT, DANIEL L. SEVERANCE, and TIMOTHY S.
ZWIER, Department of Chemistry, Purdue University, W. Lafayette, IN, 47907.

- WH5. MULTIPHOTON IONIZATION STUDIES OF CLUSTERS OF IMMISCIBLE LIQUIDS
.....Late Paper Added to Abstracts Book.....10 min.(2:33)

AARON W. GARRETT, ALBERT J. GOTCH, and TIMOTHY S. ZWIER, Department of
Chemistry, Purdue University, West Lafayette, Indiana, 47907.

- WH6. THE SPECTROSCOPY AND PHOTOPHYSICS OF 2-,4- AND 5-METHYLPYRIMIDINE
.....Late Paper Added to Abstracts Book.....10 min.(2:45)

RALPH E. BANDY, AARON W. GARRETT, JOHN NASH, and TIMOTHY S. ZWIER,
Department of Chemistry, Purdue University, West Lafayette, Indiana,
47907.

Intermission

- WH7. THE MAGNETIC ROTATION SPECTRUM OF $^{79}\text{Br}_2$ ($\text{A}^3\Pi_1 - \text{X}^1\Sigma_g^+$).....Late Paper Added
to Abstracts Book.....15 min.(3:10)

A. CHANDA, F. W. DALBY, I. OZIER, and J. SANDERS, Department of Physics,
University of British Columbia, Vancouver, British Columbia V6T 1Z1,
Canada; permanent address of Sanders: Department of Physics, University
of Oxford, Oxford, England.

- WH8. A SPECTRAL AND X-RAY STUDY OF THE $\text{Cr:Mg}_2\text{SiO}_4$ CRYSTAL...Late Paper added to
abstracts book.....10 min.(3:27)

B. C. YANG, Y. Q. LIN, P. LIN, AND I. S. CHENG, Department of Physics,
East China Normal University, Shanghai 200062, P.R. China.

- WH9. OBSERVATION OF THE $J=2$, $|k|=1$ LEVELS OF Ar-NH_3 BY FAR INFRARED DIFFERENCE
FREQUENCY - SIDEBAND SPECTROSCOPY...Late paper added to abstracts book.....15 min.(3:39)

S. W. REEVE, M. A. DVORAK, A. GRUSHOW, W. BURNS, AND K. R. LEOPOLD,
Department of Chemistry, University of Minnesota, Minneapolis,
Minnesota, 55455.

- WH10. THE $\text{C}^3\Pi$ STATE OF THE SO RADICAL...Late paper added to abstracts book.....10 min.(3:56)

C. CLERBAUX AND R. COLIN, Laboratoire de Chimie Physique Moleculaire,
Universite Libre de Bruxelles, 1050 Brussels, Belgium.

FA4 and FA5 will be presented here at the request of the author who must return
to Japan on Friday.....15 min.(4:08)
15 min.(4:25)

THURSDAY, JUNE 20, 1991 -- 8:30 A.M.

Room 1153, Physics Laboratory

Chair: ERIC HERBST, Duke University, Durham, North Carolina.

- RA1. H_2S_2 AND NH_3 : VIBRATION - ROTATION INTERACTIONS.....Invited Paper.....30 min.(8:30)
S. URBAN, Czechoslovakia Academy of Science, Prague, Czechoslovakia.
- RA2. GAS PHASE MAGNETIC VIBRATIONAL CIRCULAR DICHROISM. A POSSIBLE WAY TO DETERMINE THE ROTATIONAL g-FACTOR OF THE MOLECULAR ZEEMAN EFFECT.....15 min.(9:03)
BAOLIANG WANG and TIMOTHY A. KEIDERLING, Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois, 60680.
- RA3. INFRARED SPECTRA OF CO-H_2 AND CO-D_2 COMPLEXES IN THE 4.7 μm REGION.....15 min.(9:20)
A.R.W. MCKELLAR, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.
- RA4. FAR INFRARED SPECTRA OF HYDROGEN DIMERS: COMPARISON OF EXPERIMENT AND THEORY.....15 min.(9:37)
A.R.W. MCKELLAR, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada; and J. SCHAEFER, Max-Planck-Institut für Physik und Astrophysik, Institut für Astrophysik, D-8046 Garching, Germany.
- RA5. VARIATIONAL SEPARATION OF ANGULAR AND RADIAL MOTIONS: THE GROUND VIBRATIONAL STATE OF Ar-HCN15 min.(9:54)
DAVID YARON and WILLIAM KLEMPERER, Department of Chemistry, Harvard University, Cambridge, Massachusetts, 02138.
- RA6. MODELING THE HIGHLY EXCITED BENDING STATES, $\nu_2 = 26 \rightarrow 42$, OF X , $^1\Sigma^+$ MCP.....10 min.(10:11)
DAVID YARON, YIT-TSONG CHEN, ROBERT SILBEY, and ROBERT W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.
- Intermission
- RA7. DETERMINATION SCHEMES.....15 min.(10:35)
M. VILLA, F. J. MELENDEZ, and R. GIL, Area de Química Cuántica, Universidad Autónoma Metropolitana Iztapalapa, Av. Michoacán y la Purísima, Iztapalapa, Apartado Postal 55-532, C.P. 09340, México.
- RA8. MOLECULAR-BEAM OPTOTHERMAL SPECTROSCOPY OF THE 9.6 μm ν_{14} BAND OF BENZENE.....15 min.(10:52)
M-L. JUNTILA, J. L. DOMENECH, G. T. FRASER, and A. S. PINE, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.
- RA9. THE ν_{12} BAND OF BENZENE REVISITED.....15 min.(11:09)
J. L. DOMENECH, M-L. JUNTILA, and A. S. PINE, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.
- RA10. MOLECULAR-BEAM OPTOTHERMAL SPECTRUM OF THE OH STRETCHING BAND OF METHANOL.....15 min.(11:26)
I. KLEINER, G. T. FRASER, J. T. HOUGEN, and A. S. PINE, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

RA11. FTIR SPECTRA AND RO-VIBRATIONAL ANALYSIS OF OC10.....15 min.(11:43)

J. ORTIGOSO, R. ESCRIBANO, Instituto de Estructura de la Materia, Consejo Superior de Investigaciones Cientificas, 28006 Madrid, Spain;
J. B. BURKHOLDER, C. J. HOWARD, Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado, 80303; and
W. J. LAFFERTY, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

THE OHIO STATE UNIVERSITY INTERNATIONAL SYMPOSIUM ON MOLECULAR SPECTROSCOPY

The College of Mathematical and Physical Sciences through its Dean, and the Physics and Chemistry Departments through their respective Chairs, have expressed their strong support for the continuation of this annual conference. Please note on your calendars the dates for the 47th through the 50th of these symposia and make them a success by participating actively in all of them.

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|----------------|------------------|
| 47th Symposium | June 15-19, 1992 |
| 48th Symposium | June 14-18, 1993 |
| 49th Symposium | June 13-17, 1994 |
| 50th Symposium | June 12-16, 1995 |

The organization of these future meetings will be coordinated by a local Executive Committee with the support of Advisory Committees with substantial international representation.

ANNOUNCEMENT

Starting in 1992, a new structure will be in place for the organization of the Ohio State University International Symposium on Molecular Spectroscopy. The Ohio State Executive Committee presently consists of Terry A. Miller, Chair, Frank C. De Lucia, C. Weldon Mathews and Russell M. Pitzer. The Executive Committee is supported at Ohio State by an Administrative Liaison Committee consisting of the Dean of the College of Mathematical and Physical Sciences, the Chairs of the Physics and Chemistry Departments, and the Chair of the Executive Committee. A larger Local Coordinating Committee consists of all members of the Chemistry, Physics, and Astronomy Departments actively participating in the Symposium.

The local organization will be assisted by an International Advisory Committee consisting of a number of regular members, serving fixed terms, and annual invitees, who will balance the Committee's representation in a given year. At its first meeting last June the International Advisory Committee selected a Steering Committee to facilitate continuous interaction with the Ohio State Executive Committee with regard to detailed planning of the program for upcoming meetings. The present members of the International Advisory Committee are Jon Hougen*, Chair, NIST; Peter Bernath, University of Waterloo; Robert Field*, MIT; Guy Guelachvili, Orsay; Eizi Hirota, The Graduate University of Advanced Studies, Yokohama; John Johns*, Herzberg Institute of Astrophysics, NRC; William Klemperer, Harvard; Anthony J. Merer, University of British Columbia; John Muenster, University of Rochester; Takeshi Oka*, University of Chicago; David Pratt, University of Pittsburgh; H. M. Pickett*, JPL; Richard Saykally, UC Berkeley; Trevor Sears, Brookhaven; David Skatrud, ARO; Manfred Winnewisser and Brenda Winnewisser, Justus Liebig Universität; Claude Woods, University of Wisconsin. Those individuals marked with an asterisk are also members of the Steering Committee.

The planning for the 1992 meeting to be held June 15-19 is well advanced. The following have accepted invitations to give invited talks: Carlton Howard, NOAA, Jeremy Hutson, University of Durham, Anthony Merer, University of British Columbia, Martin Quack, ETH Zurich, and Benoit Simard, Steacie Institute of Molecular Sciences, NRC.

In addition a session will be held commemorating the many contributions of Professor K. Narahari Rao to the Symposium. Persons who will speak of Professor Rao at this session include G. Herzberg, Herzberg Institute of Astrophysics, NRC; Jon Hougen, NIST; and C. Weldon Mathews, Ohio State. The awarding of the first Rao Prizes in molecular spectroscopy will also take place at this session (see below for details). Persons wishing to have their contributed talks in 1992 in the scientific session associated with this commemoration should so indicate on their 1992 abstract.

THURSDAY, JUNE 20, 1991 -- 8:30 A.M.

Room 1009, Physics Laboratory

Chair: G. R. SUDHAKARAN, State University of New York, Oswego, New York.

- RB1. IDENTIFICATION OF B AND C-TYPE CORIOLIS INTERACTIONS IN $\lambda^1 A_u$ ACETYLENE-D₂ USING DOUBLE RESONANCE SPECTROSCOPY.....15 min.(8:30)

J. K. LUNDBERG and R. W. FIELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.

- RB2. ELECTRONIC SPECTROSCOPY OF JET-COOLED ORGANOMETALLIC FREE RADICALS PREPARED BY A LASER VAPORIZATION/PHOTOLYSIS TECHNIQUE.....15 min.(8:47)

ANDREW M. ELLIS, ERIC S. J. ROBLES, and TERRY A. MILLER, Laser Spectroscopy Facility, The Ohio State University, Columbus, Ohio, 43210.

- RB3. LASER EXCITATION SPECTROSCOPY OF ZINC AND CADMIUM CYCLOPENTADIENIDES.....10 min.(9:04)

ERIC S. J. ROBLES, ANDREW M. ELLIS, and TERRY A. MILLER, Laser Spectroscopy Facility, The Ohio State University, Columbus, Ohio, 43210.

- RB4. LASER EXCITATION SPECTROSCOPY OF THE MONOPYRROLIDE DERIVATIVES OF ZINC AND CADMIUM.....10 min.(9:16)

ERIC S. J. ROBLES, ANDREW M. ELLIS, and TERRY A. MILLER, Laser Spectroscopy Facility, The Ohio State University, Columbus, Ohio, 43210.

- RB5. LASER EXCITATION SPECTROSCOPY OF THE MONOMETHYLCYCLOPENTADIENYL COMPLEXES OF CALCIUM, ZINC AND CADMIUM.....10 min.(9:28)

ERIC S. J. ROBLES, ANDREW M. ELLIS, and TERRY A. MILLER, Laser Spectroscopy Facility, The Ohio State University, Columbus, Ohio, 43210.

- RB6. A NEW LOOK AT AN OLD MOLECULE: THE VIBRONIC SPECTROSCOPY OF p-DIFLUOROBENZENE ($-d_4$).....15 min.(9:40)

HARRY J. ELSTON, C. S. PARMENTER, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405; and FRED G. TODD, Department of Chemistry, Colorado State University, Ft. Collins, Colorado, 80523.

- RB7. THE 614 nm SUPERSONIC JET SPECTRUM OF THIOACETALDEHYDE.....15 min.(9:57)

D. C. MOULE, H. BASCAL, Department of Chemistry, Brock University, St. Catharines, Ontario L2S 3A1, Canada; D. J. CLOUTHIER, J. KAROLCZAK, Department of Chemistry, University of Kentucky, Lexington, Kentucky, 40506-0055; Y. G. SMEYERS, Instituto de Estructura de la Materia, Consejo Superior de Investigaciones, C. Serrano 119 - 28006, Madrid, Spain, and A. NINO, Escuela Universitaria de Informatica, Universidad de Castilla - La Mancha, Ronda de Calatrava s/n, Ciudad Real, 13071, Spain.

Intermission

- RB8. AXIS-SWITCHING CORRECTIONS TO THE LUSCHINSKY EFFECT.....15 min.(10:25)

TAKAMASA MOMOSE, Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan; and JON T. HOUGEN, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

- RB9. ANALYSIS OF THE PHOTOLUMINESCENCE SPECTRA OF EXCHANGE-COUPLED MO^{3+} PAIRS IN ONE-DIMENSIONAL LATTICES OF $CsMgCl_3$ AND $CsCdBr_3$15 min.(10:42)

K. MARNEY, A. FRANCIS, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109; G. MCPHERSON, Department of Chemistry, Tulane University, New Orleans, Louisiana, 70118; and P. MCCARTHY, Department of Chemistry, Canisius College, Buffalo, New York, 14208.

RB10. HIGH PRESSURE ODMR SPECTROSCOPY OF TRIPLET BENZOQUINONE SYSTEMS.....15 min.(10:59)

J. L. BABER and I. Y. CHAN, Department of Chemistry, Brandeis University,
Waltham, Massachusetts, 02254.

RB11. APPROXIMATE QUANTUM NUMBERS IN THE OPTICAL SPECTRUM OF NO_215 min.(11:16)

STEPHEN L. COY, Department of Chemistry, Massachusetts Institute of
Technology, Cambridge, Massachusetts, 02139; and KEVIN K. LEHMANN,
Department of Chemistry, Princeton University, Princeton, New Jersey,
08542.

RB12. TROPYL (C_7H_7) RADICAL ELECTRONIC STATES OBSERVED BY RESONANCE ENHANCED
MULTIPHOTON IONIZATION SPECTROSCOPY.....Arrived Late.....15 min.(11:33)

RUSSELL D. JOHNSON, III, Chemical Kinetics and Thermodynamics Division,
National Institute of Standards and Technology, Gaithersburg, Maryland,
20899.

RB13. MULTIPHOTON IONIZATION SPECTROSCOPY OF DIFLUOROMETHYL RADICALS..Arrived Late...15 min.(11:50)

JEFFREY W. HUDGENS, RUSSELL D. JOHNSON, III, BILIN P. TSAI, DAVID V.
DEARDEN, Chemical Kinetics and Thermodynamics Division, National Institute
of Standards and Technology, Gaithersburg, Maryland, 20899; and
SHERIF A. KAFABI, Department of Environmental Chemistry and Biology,
Johns Hopkins University School of Hygiene and Public Health, Baltimore,
Maryland, 21205.

THURSDAY, JUNE 20, 1991 -- 8:30 A.M.

Room 1005, Physics Laboratory

Chair: DEANNE SNAVELY, Bowling Green University, Bowling Green, Ohio

- RC1. INTERACTION OF ROTATION AND LOCAL MODE TUNNELING IN OVERTONE SPECTRA OF XH_2 MOLECULES.....Arrived Late.....15 min.(8:30)

K. K. LEHMANN, Department of Chemistry, Princeton University, Princeton, New Jersey, 08544.

- RC2. POLARIZATION SPECTROSCOPY IN THE LIMIT OF STRONG SATURATION. Arrived Late.....10 min.(8:47)

KEVIN K. LEHMANN, Department of Chemistry, Princeton University, Princeton, New Jersey, 08544; and FRANK SPANO, Department of Chemistry, Temple University, Philadelphia, Pennsylvania, 19122.

- RC3. PERTURBATIONS IN THE ν_1 AND $2\nu_1$ SPECTRA OF PROPYNE..... Arrived Late.....15 min.(8:59)

E. R. TH. KERSTEL, K. K. LEHMANN, B. H. PATE, G. SCOLES, Department of Chemistry, Princeton University, Princeton, New Jersey, 08544; A. McILROY, and D. J. NESBITT, Joint Institute for Laboratory Astrophysics, University of Colorado and National Institute of Standards and Technology, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado, 80309-0440.

- RC4. DOES A HEAVY CENTRAL ATOM REDUCE THE RATE OF VIBRATIONAL ENERGY RELAXATION?....15 min.(9:16)
(Arrived Late)

E. R. TH. KERSTEL, K. K. LEHMANN, T. F. MENTEL, B. H. PATE, and G. SCOLES, Department of Chemistry, Princeton University, Princeton, New Jersey, 08544.

- RC5. STUDY OF ENHANCED IVR IN MOLECULES WITH HINDERED INTERNAL ROTATION USING HIGH RESOLUTION INFRARED SPECTROSCOPY.....Arrived Late.....15 min.(9:33)

E. R. TH. KERSTEL, K. K. LEHMANN, T. F. MENTEL, B. H. PATE, and G. SCOLES, Department of Chemistry, Princeton University, Princeton, New Jersey, 08544.

- RC6. ROTATIONALLY RESOLVED, MOLECULAR BEAM, OVERTONE SPECTROSCOPY OF HYDROGEN-BONDED COMPLEXES: $2\nu_1$ OF $(\text{HCN})_2$ AND HCN-HFArrived Late.....15 min.(9:50)

E. R. TH. KERSTEL, T. F. MENTEL, B. H. PATE, and G. SCOLES, Department of Chemistry, Princeton University, Princeton, New Jersey, 08544.

Intermission

- RC7. RE-EXAMINATION OF THE ELECTRONIC SPECTRUM OF HCP.....Arrived Late.....15 min.(10:25)

M. A. MASON and K. K. LEHMANN, Department of Chemistry, Princeton University, Princeton, New Jersey, 08544.

- RC8. VIBRONIC STRUCTURES AND PREDISSOCIATION DYNAMICS OF TRIATOMIC CLUSTER HgAr_2Arrived Late.....10 min.(10:42)

M. OKUNISHI, Institute for Molecular Science, Okazaki 444, Japan; K. YAMANOUCHI, and S. TSUCHIYA, Department of Pure and Applied Sciences, College of Arts and Sciences, The University of Tokyo, Meguro-ku, Tokyo 153, Japan.

- RC9. LASER PHOTOELECTRON INVESTIGATION OF JET-COOLED 1,4-DIFLUOROBENZENE.....Arrived Late.....10 min.(10:54)

JOHN P. LUCIA, XINBEI SONG, and JAMES P. REILLY, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.

- RC10. TWO-COLOR PICOSECOND PHOTOELECTRON STUDY OF IVR IN ALKYLANILINE AND
ALKYLBENZENE MOLECULES.....Arrived Late.....10 min.(11:06)
XINBEI SONG, JOHN P. LUCIA, and JAMES P. REILLY, Department of
Chemistry, University of Indiana, Bloomington, Indiana, 47405.
- RC11. ADVANCES IN LOW TEMPERATURE PHOTOACOUSTIC SPECTROSCOPY: METHANE'S
 $\Delta v=4$ OVERTONE.....Arrived Late.....10 min.(11:18)
K. BORAAS and J. P. REILLY, Department of Chemistry, Indiana University,
Bloomington, Indiana, 47405.
- RC12. PHOTOACOUSTIC OVERTONE SPECTROSCOPY OF PROPYNE.....Arrived Late.....10 min.(11:30)
ZHEN LIN and J. P. REILLY, Department of Chemistry, Indiana
University, Bloomington, Indiana, 47405.
- RC13. INVESTIGATION OF DCL STRETCHING VIBRATIONS IN HYDROGEN BOND DIMERS
.....Arrived Late.....10 min.(11:42)
Z. WANG and J. W. BEVAN, Department of Chemistry, Texas A&M
University, College Station, Texas, 77843.

THURSDAY, JUNE 20, 1991 — 1:30 P.M.

Room 1153, Physics Laboratory

Chair Before Intermission: P. K. KADABA, University of Kentucky, Lexington, Kentucky.

Chair After intermission: K. W. HILLIG, II, University of Michigan, Ann Arbor, Michigan.

- RE1. SUBMILLIMETER MICROWAVE SPECTROSCOPY IN GORKY, USSR: CURRENT RESEARCH
..... Invited Paper.....30 min.(1:30)
A. F. KRUPNOV, Applied Physics Institute, USSR Academy of Science,
Gorky, USSR 603600.
- RE2. MILLIMETER AND SUBMILLIMETER SPECTRUM OF HIGHLY EXCITED STATES OF WATER.....15 min.(2:03)
J. C. PEARSON, F. C. DE LUCIA, Department of Physics, The Ohio State
University, Columbus, Ohio, 43210; T. J. ANDERSON, Department of
Chemistry, Physical Sciences, University of California-Irvine,
Irvine, California, 92717; and E. HERBST, Department of Physics,
Duke University, Durham, North Carolina, 27706.
- RE3. CYCLOPROPANE-SULFUR DIOXIDE: MICROWAVE SPECTRUM AND STRUCTURE.....10 min.(2:20)
A. M. ANDREWS, K. W. HILLIG, II, and R. L. KUCZKOWSKI, Department of
Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.
- RE4. CYCLOPROPANE-WATER: MICROWAVE SPECTRUM AND STRUCTURE.....10 min.(2:32)
A. M. ANDREWS, K. W. HILLIG, II, and R. L. KUCZKOWSKI, Department of
Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.
- RE5. INVESTIGATIONS OF LINE BROADENING AND LINE SHIFT PARAMETERS IN LOW J
ROTATIONAL TRANSITIONS OF CARBON MONOXIDE.....10 min.(2:44)
S. P. BELOV, M. YU TRETYAKOV, Institute of Applied Physics, Nizhny
Novgorod, USSR; and R. D. SUENRAM, Molecular Physics Division, National
Institute of Standards and Technology, Gaithersburg, Maryland, 20899.
- RE6. PRESSURE BROADENING OF WATER BETWEEN 80 K AND 600 K.....15 min.(2:56)
T. M. GOYETTE, F. C. DE LUCIA, Department of Physics, The Ohio State
University, Columbus, Ohio, 43210; J. M. DUTTA, and C. R. JONES,
Department of Physics, North Carolina Central University, Durham,
North Carolina, 27707.
- Intermission
- RE7. THE GROUND TORSIONAL STATE OF ACETALDEHYDE.....15 min.(3:27)
I. KLEINER, J. T. HOUGEN, R. D. SUENRAM, F. J. LOVAS, Molecular Physics
Division, National Institute of Standards and Technology, Gaithersburg,
Maryland, 20899; and M. GODEFROID, Laboratoire de Chimie Physique
Moléculaire, Université Libre de Bruxelles, CP160, 1050 Bruxelles,
Belgium.
- RE8. AN INVESTIGATION OF THE MICROWAVE SPECTRUM AND MOLECULAR STRUCTURE OF SULFONYL
CHLORIDE ISOCYANATE.....15 min(3:44)
OKSIK JO, JACK D. GRAYBEAL, Department of Chemistry, Virginia Polytechnic
Institute and State University, Blacksburg, Virginia, 24061-0212;
F. J. LOVAS, R. D. SUENRAM, Molecular Physics Division, National Institute
of Standards and Technology, Gaithersburg, Maryland, 20899.
- RE9. MICROWAVE SPECTRA OF MONOHALOGENATED ALLENES: CHLOROALLENE, BROMOALLENE,
AND IODEALLENE.....10 min.(4:01)
TERUHIKO OGATA, Faculty of Liberal Arts, Shizuoka University,
Shizuoka 422, Japan; and YUZURU NIIDE, Department of Mathematics
and Physics, National Defense Academy, Yokosuka 239, Japan.

- RE10. ROTATIONAL AND VIBRATIONAL COLLISIONAL PROCESSES IN CH_3Cl15 min.(4:13)

T. W. PAPE, Department of Physics, Duke University, Durham, North Carolina, 27706; F. C. DE LUCIA, Department of Physics, The Ohio State University, Columbus, Ohio, 43210; and D. D. SKATRUD, U. S. Army Research Office, Research Triangle Park, North Carolina, 27709.

- RE11. DIELECTRIC RELAXATION SPECTRA OF T-BUTYL ALCOHOL-WATER MIXTURE USING TIME DOMAIN REFLECTOMETRY.....10 min.(4:30)

A. C. KUMBHARKHANE, S. M. PURANIK, and S. C. MEHROTRA, Department of Physics, Marathwada University, Aurangabad, 431 001 India.

- RE12. TUNNELING INTERACTIONS BETWEEN DIFFERENT CONFORMERS IN VIBRATIONALLY EXCITED STATES OF ETHYLPHOSPHINE, $\text{CH}_3\text{CH}_2\text{PH}_2$Arrived Late.....15 min.(4:42)

P. GRONER and J. R. DURIG, Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.

- RE13. A PHYSICAL INTERPRETATION OF THE TUNNELING PARAMETERS IN THE INTERNAL AXIS TYPE TREATMENT OF LARGE AMPLITUDE MOTIONS.....Arrived Late15 min.(4:59)

P. GRONER, Department of Chemistry, University of South Carolina, Columbia, South Carolina, 29208.

THURSDAY, JUNE 20, 1991 -- 1:30 P.M.

Room 1009, Physics Laboratory

Chair: D. CHRIS BENNER, College of William and Mary, Williamsburg, Virginia.

RF1. A SIMULATION OF THE ν_4 BAND OF CHLORINE NITRATE.....10 min.(1:30)K. P. CARTEN and R. W. LOVEJOY, Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania, 18015.

RF2. HIGH RESOLUTION FT-IR SPECTROSCOPY OF TRANS-1,2-DIFLUOROETHYLENE-D2.....15 min.(1:42)

NORMAN C. CRAIG, STEPHEN C. STONE, Department of Chemistry, Oberlin College, Oberlin, Ohio, 44074; and WALTER J. LAFFERTY, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

RF3. PERFORMANCE OF A TUNABLE DIODE LASER SYSTEM WHICH UTILIZES ALL REFLECTIVE OPTICS.....10 min.(1:59)

J. BALENT and A. W. MANTZ, Department of Physics, Franklin and Marshall College, Lancaster, Pennsylvania, 17604-3003.

RF4. DATA ACQUISITION SYSTEM FOR DIODE LASER KINETIC SPECTROSCOPY AND APPLICATIONS TO HOCO AND ETHYL RADICALS.....15 min.(2:11)

PHILIP M. JOHNSON, Department of Chemistry, State University of New York, Stony Brook, New York, 11794; WAFIA M. FAWZY, and TREVOR J. SEARS, Department of Chemistry, Brookhaven National Laboratory, Upton, New York, 11973.RF5. SPECTRA OF ^{13}C ENRICHED CO_2 AT ELEVATED TEMPERATURES IN THE $15\ \mu\text{m}$ REGION.....10 min.(2:28)MARK P. ESPLIN, Stewart Radiance Laboratory, Utah State University, Bedford, Massachusetts, 01730; and MICHAEL HOKE, Geophysics Laboratory(AFSC)/OPS, Hanscom AFB, Bedford, Massachusetts, 01730.RF6. INTENSITY AND POSITION MEASUREMENTS OF CARBON DIOXIDE LINES IN THE 4370 TO $4640\ \text{cm}^{-1}$ REGION.....15 min.(2:40)L. P. GIVER and C. CHACKERIAN, JR., NASA AMES Research Center, MS 245/4, Moffett Field, California, 94035-1000.RF7. THE ν_3 , $2\nu_2$ AND ν_1 INTERACTING BANDS OF $^{14}\text{N}^{16}\text{O}_2$10 min.(2:57)A. PERRIN, A. M. VASSEROT, C. CAMY-PEYRET, J. M. FLAUD, LPMA, CNRS, Université Pierre et Marie Curie, 75252 Paris Cedex 05, France; A. GOLDMAN, Department of Physics, University of Denver, Denver, Colorado, 80208-0202; and G. GUELACHVILI, LPMA, CNRS et Université Paris-Sud, 91405 Orsay Cedex, France.

Intermission

RF8. ABSOLUTE INTENSITY AND PRESSURE BROADENING MEASUREMENTS IN THE ν_2 FUNDAMENTAL OF N_2O10 min.(3:20)J. W. JOHNS, M. NOEL, Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada; and T. L. TAN, Department of Physics, National University of Singapore, Faculty of Science, Singapore, 0511.

RF9. ABSOLUTE RAMAN INTENSITY MEASUREMENTS FOR HYDROGEN SULFIDE.....15 min.(3:32)

W. F. MURPHY and J. M. FERNÁNDEZ SÁNCHEZ, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.

RF10. THE 2.5 μ m BANDS OF OZONE: LINE POSITIONS AND INTENSITIES.....10 min.(3:49)

A. PERRIN, A.-M. VASSEROT, J.-M. FLAUD, C. CAMY-PEYRET, Laboratoire de Physique Moléculaire et Atmosphérique, Université Pierre et Marie Curie et CNRS, 75252 Paris Cedex 05, France; V. MALATHY DEVI, Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185; M.A.H. SMITH, C. P. RINSLAND, NASA Langley Research Center, Atmospheric Sciences Division, Mail Stop 401A, Hampton, Virginia, 23665-5225; A. BARBE, S. BOUAZZA and J. J. PLATEAUX, Laboratoire de Physique Moléculaire, U.A. CNRS 776, Université de Reims, 51062 Reims Cedex, France.

RF11. THE ν_2 BANDS OF THE MONOSUBSTITUTED ^{17}O -SPECIES OF OZONE.....10 min.(4:01)

A. PERRIN, C. CAMY-PEYRET, J.-M. FLAUD, Laboratoire de Physique Moléculaire et Atmosphérique, Université Pierre et Marie Curie et CNRS, 75252 Paris Cedex 05, France; C. P. RINSLAND, M.A.H. SMITH, Atmospheric Sciences Division, NASA Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665-5225; and V. MALATHY DEVI, Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185.

RF12. H. R. INFRARED SPECTRUM OF $^{18}\text{O}_3$: ANALYSIS OF THE TRIAD $2\nu_1$, $\nu_1+\nu_3$ AND $2\nu_3$15 min.(4:13)

A. BARBE, S. BOUAZZA, J. J. PLATEAUX, Université de Reims, URA 1434, UFR Sciences, 51062 Reims Cedex, France; J. F. FLAUD, and C. CAMY-PEYRET, Laboratoire de Physique Moléculaire et Atmosphérique, Université Pierre et Marie Curie et CNRS, 75252 Paris Cedex 05, France.

RF13. THE ν_4 BAND OF CARBONYL FLUORIDE.....10 min.(4:30)

J. M. FLAUD, C. CAMY-PEYRET, Laboratoire de Physique Moléculaire et Atmosphérique, Université Pierre et Marie Curie et CNRS, 75252 Paris Cedex 05, France; A. GOLDMAN, F. J. MURCRAY, R. D. BLATHERWICK, Department of Physics, University of Denver, Denver, Colorado, 80208-0202; and C. P. RINSLAND, Atmospheric Sciences Division, NASA Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665-5255.

RF14. AN ANALYSIS OF THE FAR INFRARED SPECTRUM OF ACETONE.....15 min.(4:42)

Y. G. SMEYERS, M. L. SENENT, Instituto de Estructura de la Materia, Consejo Superior de Investigaciones, C. Serrano 119 - 28006, Madrid, Spain; and D. C. MOULE, Department of Chemistry, Brock University, St. Catharines, Ontario L2S 3A1, Canada.

RF15. INFRARED DIODE LASER AND FOURIER TRANSFORM SPECTROSCOPY OF A LOW PRESSURE PREMIXED GAS FLAME.....Late Paper Added to Abstracts Book.....10 min.(4:59)

K. L. MCNESEY and R. A. FIFER, U. S. Army Ballistic Research Laboratory, Attn: SLCBR-IB-1, Aberdeen Proving Ground, Maryland, 21005-5066.

THURSDAY, JUNE 20, 1991 — 1:30 P.M.

Room 1005, Physics Laboratory

Chair: N. C. HANDY, University of Cambridge, Cambridge, England.

- RG1. LOW ENERGY ELECTRON-SILANE SCATTERING USING THE COMPLEX KOHN METHOD AND POLARIZED ORBITALS.....15 min.(1:30)

WEIGUO SUN, C. W. McCURDY, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210; and B. H. LENGFIELD III, Lawrence Livermore National Laboratory, Livermore, California, 94550.

- RG2. ELECTRONIC STRUCTURE OF HCCO RADICAL.....15 min.(1:47)

KYUNGSUN KIM and ISAIAH SHAVITT, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

- RG3. AN AB INITIO METHODOLOGICAL STUDY OF THE STRUCTURES AND EXCITATION ENERGIES OF THE (n, π^*) STATES OF N_2H_215 min.(2:04)

KYUNGSUN KIM, ISAIAH SHAVITT, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210; and JANET E. DEL BENE, Department of Chemistry, Youngstown State University, Youngstown, Ohio, 44555.

- RG4. AN AB INITIO STUDY OF $n \rightarrow \pi^*$ TRANSITION ENERGIES IN HYDROGEN-BONDED COMPLEXES...15 min.(2:21)

J. E. DEL BENE, Department of Chemistry, Youngstown State University, Youngstown, Ohio, 44555; E. A. STAHLBERG, and I. SHAVITT, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

- RG5. AN AB INITIO STUDY OF THE SO_2 ELECTRONIC SPECTRA IN THE 3900-1750 Å REGION.....15 min.(2:38)

R. J. ZELLMER and I. SHAVITT, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

- RG6. TORSION-ROTATION PERTURBATIONS IN ELECTRONIC SPECTROSCOPY. THE $S_1 \rightarrow S_0$ SPECTRUM OF 2-METHYL-1-NAPHTHOL.....15 min.(2:55)

X.-Q. TAN, Department of Physics, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260; and D. W. PRATT, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania, 15260.

Intermission

- RG7. AB INITIO AND MODEL STUDIES OF WEAKLY BONDED CLUSTERS OF CARBON MONOXIDE.....15 min.(3:25)

C. A. PARISH, C. E. DYKSTRA, J. D. AUGSPURGER, Department of Chemistry, Indiana University-Purdue University, Indianapolis, Indiana, 46205.

- RG8. AB INITIO CALCULATIONS OF DIRHENIUM COMPLEXES USING RELATIVISTIC EFFECTIVE CORE POTENTIALS.....15 min.(3:42)

J. P. BLAUDEAU, R. ROSS, R. PITZER, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210; P. MOUGENOT, and M. BENARD, Laboratoire de Chimie Quantique, E.R. 139 du CNRS, Institut Le Bel, Université Louis Pasteur, 67000 Strasbourg, France.

- RG9. COPPER CHLORIDE: SPIN-ORBIT CI POTENTIAL CURVES.....15 min.(3:59)

NORA M. WALLACE and RUSSELL M. PITZER, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

- RG10. ELECTRONIC STRUCTURES OF $Np(C_8H_8)_2$ AND $Pu(C_8H_8)_2$15 min.(4:16)

AGNES H. H. CHANG and RUSSELL M. PITZER, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

RG11. SPIN-ORBIT CI STUDY OF VALENCE AND RYDBERG STATES OF LiBe.....15 min.(4:33)

M. M. MARINO, C. W. KERN, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210; W. C. ERMILER, Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey, 07030; and V. E. BONDYBEY, Institute für Physikalische Chemie der T. U. München, 8046 Garching, Germany and Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

RG12. AB INITIO SPIN-ORBIT CONFIGURATION INTERACTION CALCULATIONS ON THE Li₂Be CLUSTER.....15 min.(4:50)

M. AKBULUT, Department of Physics, Stevens Institute of Technology, Hoboken, New Jersey, 07030; and W. C. ERMILER, Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey, 07030.

FRIDAY, JUNE 21, 1991 -- 8:30 A.M.

Room 1153, Physics Laboratory

Chair: T. M. GOYETTE, The Ohio State University, Columbus, Ohio.

- FA1. ROTATIONAL SPECTRUM, STRUCTURE, AND DIPOLE MOMENT OF THE $\text{SiF}_4\text{-NH}_3$ SYMMETRIC TOP.....15 min.(8:30)
R. S. RUOFF, T. J. Watson Research Center, IBM, Yorktown Heights, New York, 10598; T. EMILSSON, A. I. JAMAN, T. C. GERMANN, and H. S. GUTOWSKY, Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois, 61801.
- FA2. MICROWAVE ROTATIONAL SPECTRUM AND ELECTRICAL PROPERTIES OF Kr-BENZENE.....15 min.(8:47)
T. D. KLOTS, Chemistry Division, Argonne National Laboratory, Argonne, Illinois, 60439; T. EMILSSON, and H. S. GUTOWSKY, Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois, 61801.
- FA3. $K=0$ TRANSITIONS IN THE ROTATIONAL SPECTRUM OF Ar-HCN.....10 min.(9:04)
T. C. GERMANN, T. EMILSSON, and H. S. GUTOWSKY, Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois, 61801.
- FA4. MICROWAVE SPECTRUM OF NaBH_4FA4 and FA5 have been rescheduled at end of Session WH
Y. KAWASHIMA, Kanagawa Institute of Technology, 1030 Shimo-ogino, Atsugi, Kanagawa 243-02, Japan; C. YAMADA, and E. HIROTA, Institute for Molecular Science, Okazaki, 444, Japan.
- FA5. MICROWAVE SPECTRUM OF LiBH_4
Y. KAWASHIMA, Kanagawa Institute of Technology, 1030 Shimo-ogino, Atsugi, Kanagawa 243-02, Japan; and E. HIROTA, Institute for Molecular Science, Okazaki, 444, Japan and the Graduate University for Advanced Studies, Midori-ku, Yokohama 227, Japan.
- FA6. THE ARGON-FORMIC ACID VAN DER WAALS COMPLEX.....10 min.(9:50)
I. I. IOANNOU, K. W. HILLIG II, and R. L. KUCZKOWSKI, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.
 Intermission (rescheduled after FA8)
- FA7. DIPOLE MOMENTS OF THE OCS-Ne , OCS-Ar AND OCS-Kr VAN DER WAALS COMPLEXES.....10 min.(10:15)
L. NEMES, Research Laboratory for Inorganic Chemistry, Hungarian Academy of Sciences, H-1502 Budapest, Hungary; S. L. MARUCA, A. M. ANDREWS, K. W. HILLIG II, and R. L. KUCZKOWSKI, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, 48109.
- FA8. THE ν_4 FUNDAMENTAL BANDS OF TRANS AND CIS- HNO_210 min.(10:27)
I. KLEINER, Molecular Physics Division, National Institute for Standards and Technology, Gaithersburg, Maryland, 20899; J. M. GUILMOT, M. CARLEER, and M. HERMAN, Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles, 1050 Bruxelles, Belgium.
- FA9. MICROWAVE SPECTRUM AND STRUCTURE OF $\text{CH}_3\text{CN-BF}_3$15 min.(10:39)
M. A. DVORAK, K. R. LEOPOLD, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, 55455; R. S. FORD, university of Minnesota-Morris, Morris, Minnesota, 56267; F. J. LOVAS, and R. D. SUENRAM, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.
- FA10. MICROWAVE CHARACTERIZATION OF POLY-PARA-PHENYLENE-BENZOBIS-THIAZOLE(PBT).....10 min.(10:56)
J. CAMPBELL, H. HEJASE, P. K. KADABA, Department of Electrical Engineering, University of Kentucky, Lexington, Kentucky, 40506-0055; and K. NAISHADAM, Department of Electrical Engineering, Wright State University, Dayton, Ohio, 45435.

FA11. THE MICROWAVE SPECTRUM OF CYCLOPENTADIENYL-COBALT-DICARBONYL.....10 min.(11:08)

S. G. KUKOLICH, M. A. ROEHRIG, QI-QI CHEN, S. T. HAUBRICH, Department of Chemistry, The University of Arizona, Tucson, Arizona, 85721; and R. E. BUMGARNER, Division of Geological and Planetary Sciences 170-25, California Institute of Technology, Pasadena, California, 91125.

FA12. MICROWAVE MEASUREMENTS OF COBALT AND NITROGEN QUADRUPOLE COUPLING IN $\text{Co}(\text{CO})_3\text{NO}$10 min.(11:20)

M. A. ROEHRIG, S. G. KUKOLICH, S. T. HAUBRICH, and J. A. SHEA, Department of Chemistry, University of Arizona, Tucson, Arizona, 85721.

FA13. DETERMINATION OF THE STRUCTURES OF THE CONFORMATIONS OF DIPROPYL ETHERLate Paper Added to Abstracts Book.....10 min.(11:32)

KIMBERLEY J. GRANT, A. R. HIGHT, STEWART E. NOVICK, Department of Chemistry, Wesleyan University, Middletown, Connecticut, 06459; and ROBERT K. BOHN, Department of Chemistry, University of Connecticut, Storrs, Connecticut, 06269-3060.

* * * * *

Rao Prize

Starting at the 1991 meeting three prizes (consisting of an autographed copy of one of G. Herzberg's books) will be awarded to students who are presenting their first talk at a scientific meeting. Candidates must be certified by a letter (received by Professor Terry A. Miller at Ohio State prior to May 10, 1991) from their research supervisor as: (i) primary author of the work being presented; (ii) the actual presenter of the talk, (iii) never having delivered a spoken talk (as opposed to a poster) at a major scientific meeting (iv) not having completed a Ph.D. thesis prior to March 1, 1991. The letter of certification from the research supervisor is not a nomination letter and *will not* be considered by the prize judges. The prizes will be awarded during a plenary session of the 1992 Symposium and the winners will be cited in the Abstract Book. This prize was created by a group of spectroscopists who, as graduate students, benefited from the emphasis on graduate student participation, which has been a unique characteristic of the Symposium on Molecular Spectroscopy. To make a tax-deductible donation towards the future of the prize, please send a check, payable to The Ohio State University, to Terry A. Miller, Department of Chemistry, 120 W. 18th Ave., The Ohio State University, Columbus, Ohio 43210. The award will be administrated in 1991 by a Prize Committee consisting of Robert W. Field, Chair, M.I.T; John Muentner, Rochester; David Pratt, Pittsburgh; and Trevor Sears, Brookhaven. Any questions or suggestions about the Prize should be addressed to the Committee. Anyone (especially postdocs) willing to serve as a member of a panel of approximately 10 judges should contact Robert Field.

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FRIDAY, JUNE 21, 1991 -- 8:30 A.M.

Room 1009, Physics Laboratory

Chair: C. WELDON MATHEWS, The Ohio State University, Columbus, Ohio.

FB1. SUGGESTED GROUND STATE FREQUENCY AND BOND ENERGY FOR NiF.....15 min.(8:30)

T. C. DEVORE, Department of Chemistry, James Madison University,
Harrisonburg, Virginia, 22807; M. MCQUAID, and J. L. GOLE, School
of Physics, Georgia Institute of Technology, Atlanta, Georgia,
30332.

FB2. LASER SPECTROSCOPY OF VIBRATIONALLY-EXCITED RYDBERG STATES OF H₃.....15 min.(8:47)

L. J. LEMBO, TRW, 1 Space Park, Redondo Beach, California, 90278;
H. HELM, and D. L. HUESTIS, Molecular Physics Laboratory, SRI
International, Menlo Park, California, 94025.

FB3. INFRARED LASER SPECTROSCOPY OF THE C₂H RADICAL.....15 min.(9:04)

Y-B. YAN and T. AMANO, Herzberg Institute of Astrophysics, National
Research Council, Ottawa, Ontario K1A 0R6, Canada.

FB4. STIMULATED EMISSION PUMPING SPECTROSCOPY OF JET COOLED NCO.....15 min.(9:21)

F. J. NORTHRUP, TREVOR J. SEARS, and MING WU, Department of Chemistry,
Brookhaven National Laboratory, Upton, New York, 11973.

FB5. INFRARED FLASH KINETIC SPECTROSCOPY OF THE KETENYL RADICAL.....15 min.(9:38)

KENNETH G. UNFRIED, GHAHAM P. GLASS, and R. F. CURL, Department of
Chemistry, Rice University, Houston, Texas, 77251.

FB6. INFRARED DIODE LASER ABSORPTION SPECTROSCOPY OF HOCO.....15 min.(9:55)

WAFAA M. FAWZY and TREVOR J. SEARS, Department of Chemistry, Brookhaven
National Laboratory, Upton, New York, 11973.

FB7. DIRECT ABSORPTION SPECTROSCOPY OF CARBON CLUSTERS IN THE VISIBLE REGION.....15 min.(10:12)

F. SCAPPINI, Istituto di Spettroscopia Molecolare del CNR, 40126
Bologna, Italy; W-B. YAN, and T. AMANO, Herzberg Institute of
Astrophysics, National Research Council, Ottawa, Ontario K1A 0R6,
Canada.

Intermission

FB8. STARK SPECTROSCOPY OF ¹³CD₃OH AND CH₃OD WITH THE HCN LASER.....15 min.(10:40)

G. R. SUDHAKARAN, Department of Physics, State University of New York
at Oswego, Oswego, New York, 13126; R. M. LEES, Department of Physics,
University of New Brunswick, Fredericton, New Brunswick E3B 5A3,
Canada; R. L. BHATTACHARJEE, Department of Chemistry, University of
Rochester, Rochester, New York, 14627; and T. MUKHOPADHYAY,
Center for Advanced Technology, Rajendranagar, Indore 452012,
India.

FB9. THE JET-COOLED FLUORESCENCE EXCITATION SPECTRUM AND RING-BENDING POTENTIAL
ENERGY FUNCTION AND CONFORMATION OF 2-CYCLOPENTEN-1-ONE IN THE S₁(n,π*)
ELECTRONIC EXCITED STATE.....15 min.(10:57)

C. M. CHEATHAM and JAAN LAANE, Department of Chemistry, Texas A&M
University, College Station, Texas, 77843.

FB10. DESIGN AND OPERATION OF A SUPERSONIC JET AND LASER-INDUCED FLUORESCENCE
EXCITATION APPARATUS FOR ANALYSIS OF VIBRATIONAL LEVELS IN ELECTRONIC
EXCITED STATES.....15 min.(11:14)

M. CHEATHAM, J. ZHANG, M. HUANG, N. MEINANDER, M. B. KELLY, P. SAGEAR,
and J. LAANE, Department of Chemistry, Texas A&M University, College
Station, Texas, 77843.

- FB11. LASER-INDUCED FLUORESCENCE SPECTROSCOPY OF THE INERT GAS MOLECULAR RADICAL VAN DER WAALS COMPLEXES $X\text{-CdCH}_3$ ($X = \text{He, Ne, Ar, Kr, AND Xe}$).....15 min.(11:31)
ANDREW M. ELLIS, ERIC S. J. ROBLES, and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.
- FB12. HIGH RESOLUTION SPECTROSCOPY OF BENZYL AND RELATED RADICALS.....10 min.(11:48)
 TAI-YUAN DAVID LIN, TIMOTHY M. CERNY, JAMES M. WILLIAMSON, and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.
- FB13. DETERMINATION OF VIBRONIC DEGENERACY LIFTING AND JAHN-TELLER DISTORTION IN ASYMMETRICALLY DEUTERATED CYCLOPENTADIENYL RADICALS BY HIGH RESOLUTION LASER SPECTROSCOPY.....15 min.(12:00)
LIAN YU, DAVID W. CULLIN, JAMES M. WILLIAMSON, and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.
- FB14. ROTATIONALLY RESOLVED LASER INDUCED FLUORESCENCE SPECTROSCOPY OF FREE RADICAL-INERT GAS COMPLEXES: $\text{C}_5\text{H}_5\cdots\text{He}$, $\text{C}_5\text{H}_5\cdots\text{He}_2$, $\text{C}_5\text{H}_5\cdots\text{Ne}$ AND $\text{CH}_3\text{-C}_5\text{H}_4\cdots\text{He}_2$15 min.(12:17)
LIAN YU, JAMES M. WILLIAMSON, DAVID W. CULLIN, and TERRY A. MILLER, Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

FRIDAY, JUNE 21, 1991 -- 8:30 A.M.

Room 1075, Physics Laboratory

Chair: M. C. HEAVEN, Emory University, Atlanta, Georgia.

- FC1. A VAN DER WAALS COMPLEX STUDY OF THE ORIENTATION DEPENDENCE IN COLLISIONAL RELAXATION OF GLYOXAL(S_1) BY Ar.....15 min.(8:30)
LUC LAPIERRE and HAI-LUNG DAI, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, 19104-6323.
- FC2. A COMPARISON OF EXPERIMENTAL AND AB INITIO CROSS SECTIONS FOR ROTATIONALLY AND VIBRATIONALLY INELASTIC SCATTERING FROM S_1 GLYOXAL IN COLLISIONS WITH He...15 min.(8:47)
K. W. BUTZ, Department of Chemistry, School of Science, Griffith University, Nathan QLD 4111, Australia; H. DU, Chemistry Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, Illinois, 60439; B. D. GILBERT, C. S. PARMENTER, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405; and D. KRAJNOVICH, IBM Almaden Research Center, 650 Harry Road, San Jose, California, 95120.
- FC3. PHOTOLYSIS OF CH_3COOD IN THE FIRST $^1(n,\pi^*)$ BAND.....10 min.(9:04)
D. R. PETERMAN and J. A. GUEST, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, 45221-0172.
- FC4. EFFECT OF CLUSTERING ON ELECTRONIC RADIATIONLESS DECAY: THE SUPPRESSION OF "CHANNEL THREE" IN BENZENE COMPLEXES.....15 min.(9:16)
M. Y. HAHN, P. Y. CHENG, S. S. JU, and HAI-LUNG DAI, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, 19104.
- FC5. METHYL ROTOR ACCELERATION OF VAN DER WAALS BOND DISSOCIATION. A SPECTROSCOPIC VIEW.....15 min.(9:33)
Z. Q. ZHAO and C. S. PARMENTER, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405.
- FC6. TIME RESOLVED MEASUREMENTS OF STATE RESOLVED COLLISIONAL ENERGY TRANSFER IN THE ELECTRONIC GROUND STATE OF NH_3 WITH IR-DOUBLE(TRIPLE)-RESONANCE SPECTROSCOPY.....15 min.(9:50)
B. ABEL, S. L. COY, J. J. KLAASSEN, and J. I. STEINFELD, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139.
- Intermission
- FC7. TRANSLATIONAL ENERGY STUDY OF CH_3 PHOTOFRAGMENTS RESULTING FROM 266-NM EXCITATION OF ACETONE.....15 min.(10:20)
L. D. WAITS, R. J. HORWITZ, and J. A. GUEST, Department of Chemistry, University of Cincinnati, Cincinnati, Ohio, 45221-0172.
- FC8. VIBRATIONAL RELAXATION OF OZONE IN O_3-O_2 AND O_3-N_2 GAS MIXTURES FROM INFRARED DOUBLE-RESONANCE MEASUREMENTS.....10 min.(10:37)
F. MENARD, L. DOYENNETTE, J. MENARD, and J. M. FLAUD, Laboratoire de Physique Moléculaire et Atmosphérique, Université Pierre et Marie Curie et CNRS, 75252 Paris Cedex 05, France.
- FC9. INFRARED SPECTROSCOPY OF HIGHLY VIBRATIONALLY EXCITED $HOCH$, $HONO_2$ AND $(CH_3)_3COOH$15 min.(10:49)
P. R. FLEMING, M. LI, and T. R. RIZZO, Department of Chemistry, University of Rochester, Rochester, New York, 14627.

- FC10. INFRARED-OPTICAL DOUBLE RESONANCE SPECTROSCOPY OF THE (4,1) LOCAL-LOCAL OH STRETCH COMBINATION BAND OF HOOH.....15 min.(11:06)

X. LUO and T. R. RIZZO, Department of Chemistry, University of Rochester, Rochester, New York, 14627.

- FC11. CONTRASTING EIGENSTATE BEHAVIOR IN THE METHYL STRETCH REGIONS OF 1-BUTYNE AND ETHANOL: EVIDENCE FOR CORIOLIS AND/OR CENTRIFUGAL IVR MECHANISMS IN ETHANOL...15 min.(11:23)

G. A. BETHARDY, J. GO, and D. S. PERRY, Department of Chemistry, University of Akron, Akron, Ohio, 44325.

- FC12. ENERGY TRANSFER PROPERTIES OF THE LOWEST EXCITED ELECTRONIC STATE OF CO: $a^3\Pi_J$Late Paper Added to Abstracts Book.....15 min.(11:40)

C. A. ROGASKI, J. M. PRICE, and A. M. WODTKE, Department of Chemistry, University of California, Santa Barbara, California, 93106.

MA1

STRATOSPHERIC SPECTROSCOPY: UARS AND BEYOND. 35 min.
(UARS = Upper Atmospheric Research Satellite)

HERBERT M. PICKETT, Jet Propulsion Laboratory, California Institute of Technology,
Pasadena California, 91109

MA2

MILLIMETER AND SUBMILLITER WAVE SPECTROSCOPY
OF REACTIVE SPECIES. 35 min.

CLAIRE DEMUYNCK, Laboratoire de Spectroscopie Hertzienne, Université de
Lille-Flandres-Artois, CNRS, 59655 Villeneuve d'Ascq, France.

MA3

HIGH RESOLUTION MICROWAVE FOURIER TRANSFORM AND STARK EFFECT STUDIES OF
SMALL NITROGEN COMPOUNDS

DIETER H. SUTTER

Christian-Albrechts-Universität, Kiel, Germany

Within the last decade microwave Fourier transform spectroscopic techniques combined with molecular beam techniques have improved the resolution in routine rotational spectroscopy by two orders of magnitude. Are cw-spectrometers based on Stark effect modulation now obsolete?

After a short introduction to the basic principles of microwave Fourier transform spectroscopy, the advantages and disadvantages of the different types of spectrometers will be discussed on the basis of experiences gained with instruments developed by the Kiel group.

As an example experimental studies of small imine-, nitro- and nitrile-compounds will be presented and their results will be compared with the corresponding results from quantum chemical calculations. Quantum chemists may feel challenged!

D. H. Sutter, Abteilung Chemische Physik im Institut für Physikalische Chemie der Christian-Albrechts-Universität zu Kiel, Ludwig-Meyn Str. 4, D-2300 Kiel 1, Federal Republic of Germany

Intermission

COBLENTZ PRIZE AND AWARD LECTURE

MA4

CHEMISTRY AND SPECTROSCOPY AT MATERIALS INTERFACES: WHAT WE KNOW
AND KNOW NOT. P.W. BOHN

An important problem in modern materials chemistry involves the structure and order of molecules at interfaces between materials of differing composition. These systems comprise an especially challenging problem to the molecular spectroscopist, since there are typically only a small number of molecules exerting an inordinately large influence on the properties of the structure, the concept of order is far different than it is in macroscopic systems, and the interface may be buried and not available for direct examination.

These problems have been attacked in our laboratory by exploiting the special properties of integrated optical structures and coupling them to a variety of different spectroscopic probes. Orientations of molecules at dielectric surfaces can be obtained from careful measurements of linear dichroic ratios excited by high-order eigenmodes in Ti:Zn glass waveguides. These measurements have been applied while perturbing monolayers with various external forces and have taught us a great deal about the response of two-dimensional molecular systems to these perturbations. Raman scattering from monolayers of molecules at dielectric surfaces has been achieved in composite systems comprised of layered oblate noble metal ellipsoids and sputtered oxides. These experiments have taught us a great deal about intermolecular interactions and their response to external perturbations. A new set of measurements is using fluorescence anisotropy in these monolayer systems to characterize the distribution of orientations obtained. Finally by paying careful attention to the electric field amplitude distributions in integrated optical structures, it has even been possible to perform optical depth profiling experiments.

Despite the successes achieved through the use of integrated optical structures, a number of very challenging and important problems remain to be solved. For example, much of what is currently known about the interaction of light and molecules on surfaces rests on the use of a macroscopic description. A macroscopic description of the local field present at an interface is a necessity to obtain reliable absolute measurements of structure. In addition we are still lacking a probe which has the power of nmr for determining intermolecular interactions at interfaces. Thus, while much has been learned, there remains much to do.

Address: Department of Chemistry and Beckman Institute, University of Illinois at Urbana-Champaign, 1209 W. California St., Urbana, Illinois 61801

ME1 (1:30)

THE INFRARED SPECTRUM OF Ar-HCCH REVISITED

T. A. Hu, Ling Hong Sun, and J. S. Muentert

The infrared spectrum of the argon-acetylene van der Waals complex has been re-investigated in the three micron wavelength region. Two bands, corresponding to the ν_3 and $\nu_2+\nu_4+\nu_5$ Fermi diad of the monomer, have been recorded. The infrared data were combined with recently published ground state microwave data in a least squares analysis using the Watson S reduction of the asymmetric top Hamiltonian. Some general features of the rotational constants obtained include: very large, positive inertial defects; a large decrease in A on going from the ground to the excited vibrational states; and inverted $K=2$ asymmetry doublets in the excited states. This last feature, where the $J_{2,1-1}$ energy levels lie above the $J_{2,1-2}$ levels, is caused by $d_2 = -0.18$ MHz. All of these features are related to large amplitude motions, which are being analyzed in a dynamic model which couples internal rotation of the HCCH monomer with the overall rotation of the complex.

Address of Hu, Sun, and Muentert: Dept. of Chemistry, University of Rochester, Rochester, N.Y. 14627.

ME2 (1:47)

THE DIPOLE MOMENT OF CO₂-CO

Ratan Bhattacharjee, Michael Szafranski, and J. S. Muentert

Dipole moment measurements for a number of van der Waals complexes made up of non-polar constituents have been made, giving results ranging from 0.03 D to 0.5 D. However, the signs of these induced dipole moments have not been determined. The sign of the induced dipole moment can be determined for a complex which contains a monomer having a small dipole moment of known sign. Complexes containing a non-polar molecule and carbon monoxide provide the means to study induced moments with relatively few effects from internal motions. The dipole moment of CO₂-CO has been obtained from radio frequency transitions measured using molecular beam electric resonance spectroscopy. A 20 v/cm electric field is sufficient to produce a 1 MHz Stark shift in the $2_{20} \rightarrow 2_{21}$ transition. The dipole moment from these measurements is $\mu = 0.2493$ D. Combining this result with the CO moment of $\mu = 0.1098$ gives an induced moment in the CO₂-CO complex of 0.1395 D. The orientation of the induced moment is in the same direction as that of the CO moment, which makes the CO₂ monomer positive relative to the CO monomer. Calculations using a distributed polarizability model are currently in progress.

Address of Bhattacharjee, Szafranski, and Muentert: Dept. of Chemistry, University of Rochester, Rochester, N.Y. 14627.

ME3 (1:59)

DISSOCIATION OF SMALL METHANOL CLUSTERS AFTER EXCITATION OF THE O-H STRETCH VIBRATION AT 2.7 μ .

A. KULCKE, F. HUISKEN, C. LAUSH, AND J. M. LISY

Molecular beam depletion spectroscopy has been utilized to study the O-H stretching vibrations in methanol dimer. A Nd:YAG laser pumped optical parametric oscillator has provided tunable infrared radiation in the 2.7 μ range to dissociate methanol dimer without contamination from larger clusters. Two absorptions have been observed at 3574.4 and 3684.1 cm⁻¹. The lower frequency band represents a red shift of 106.6 cm⁻¹ from the monomer absorption and can be assigned to the excitation of the proton donor O-H stretch in the hydrogen bonded dimer. Measurement of the integrated absorption cross-section indicates a substantial enhancement in the proton donor relative to the monomer value.

Address of Kulcke and Huysken: Max-Planck-Institut für Strömungsforschung, Bunsenstrasse 10, D-3400 Göttingen, FRG.

Address of Laush and Lisy: Department of Chemistry, University of Illinois, Urbana, Illinois 61801.

ME4 (2:16)

SPECTROSCOPY AND RELAXATION OF I_2-Ar_n CLUSTERS: GEMINATE RECOMBINATION WITHIN SMALL GAS PHASE CLUSTERS.

J. Tellinghuisen, S. Fei, X. Zheng, and M. C. Heaven

Small I_2-Ar_n clusters were generated by supersonic expansion of I_2/Ar mixtures. Pulsed 193nm excitation was used to excite the ion-pair states of I_2 within the clusters. Upon excitation, the clusters emitted a broad band centered around 400nm. This feature was assigned to the D'-A' transition of I_2-Ar_n . Interaction with the Ar "cage" red-shifted the transition by more than $4000cm^{-1}$ from the gas phase position. The metastability of $I_2(A')$ within the clusters was demonstrated by using a pulsed dye laser to re-excite the D'-A' transition. Intense LIF spectra were obtained 10 μ s after the 193nm pulse.

532nm excitation was used to photolyse I_2 within the clusters. $I_2(A')$, formed by geminate recombination, was detected by laser excitation of the D'-A' transition. Both clustered and free $I_2(A')$ were observed. These results and qualitative models of the dynamical processes will be presented.

Address of Tellinghuisen: Department of Chemistry, Vanderbilt University, Nashville, TN 37235.

Address of Fei, Zheng, and Heaven: Department of Chemistry, Emory University, Atlanta GA 30322.

ME5 (2:33)

SPECTROSCOPY AND PREDISSOCIATION DYNAMICS OF $OH/D-Ne A^2\Sigma^+$.

S. Fei, X. Zheng, Y. Lin, and M. C. Heaven

We have previously reported the observation and analysis of several bands belonging to the $OH/D-Ne A-X$ systems¹. These were all associated with the 0 - 0 transitions of OH or OD. More recently, bands associated with the 1 - 0 and 2 - 1 transitions have been observed. Preliminary analyses of these data indicate that the $OH/D-Ne$ interaction is weakly perturbed by vibrational excitation of the O-H/D stretch.

Wavelength-resolved fluorescence spectra show that $OH/D(A, v' = 1)-Ne$ complexes undergo vibrational predissociation. Most of the bands involving excitation of the $-Ne$ stretching motion dissociated to leave the OH/D fragments in specific rotational states ($N' = 12$ for OH; $N' = 15$ for OD). Time-resolved measurements yielded vibrational predissociation rates in the range of $2-7 \times 10^5 s^{-1}$. Lifetime measurements for $OH(A, v'=2)-Ne$ indicate that electronic predissociation of OH is inhibited by the presence of the Ne atom.

Analyses of the spectroscopic and kinetic data will be presented. Correlations between the predissociations of the complexes and the relaxation dynamics of $OH/D(A)$ isolated in solid Ne will be discussed.

1. Y. Lin, S. K. Kulkarni, and M. C. Heaven, J. Phys. Chem. **94**, 1720 (1990).

Address of Fei, Zheng, Lin, and Heaven: Department of Chemistry, Emory University, Atlanta, GA 30322.

ME6 (2:50)

MICROWAVE AND INFRARED SPECTRA OF $C_2H_4 \cdots HCCH$

G. T. FRASER, F. J. LOVAS, R. D. SUENRAM, J. Z. GILLIES, AND C. W. GILLIES

Microwave spectra of $C_2H_4 \cdots HCCH$, $C_2H_4 \cdots DCCH$, $C_2H_4 \cdots DCCD$, $D_2C=CH_2 \cdots HCCH$, and trans-HDC=CHD \cdots HCCH have been recorded using a pulsed-nozzle Fourier-transform microwave spectrometer. An a -type, $\Delta K_a = 0$ spectrum is observed, with a number of transitions being split into doublets due to tunneling. For the normal isotopic species we find $A = 25981(33)$ MHz, $B+C = 3478.2560(13)$ MHz, and $B-C = 89.45(18)$ MHz. The complex is shown to have a C_{2v} structure in which the HCCH unit hydrogen bonds to the ethylene π cloud, with the HCCH axis normal to the plane of the ethylene. The hydrogen-bond length is found to be 2.78 Å. Centrifugal-distortion analysis yields a weak-bond stretching force constant of 0.025 mdyne/Å, corresponding to a stretching frequency of 56 cm^{-1} . Stark effect measurements determine the electric dipole moment of the complex to be 0.2654(6) D. An infrared spectrum of the asymmetric acetylenic C-H stretch in the complex has also been measured using an color-center laser optothermal spectrometer. The rotational lines are predissociation broadened, preventing the resolution of K structure. The Q-branch for the band overlaps the Q-branch for the equivalent band in the acetylene dimer.

Address of Fraser, Lovas, and Suenram: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

Address of J. Z. Gillies: Department of Chemistry, Siena College, Loudonville, NY 12221.

Address of C. W. Gillies: Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180.

Intermission

ME7 (3:20)

OPTHOTHERMAL-DETECTED MICROWAVE-SIDEBAND CO_2 -LASER SPECTROSCOPY OF $NCH-NH_3$

G. T. FRASER, A. S. PINE, W. A. KREINER*, AND R. D. SUENRAM

A microwave-sideband CO_2 laser is used together with an electric-resonance optothermal spectrometer to measure the infrared spectrum of the NH_3 umbrella vibration in $NCH-NH_3$ at a resolution of ~3 MHz. The infrared radiation is produced by mixing Lamb-dip-stabilized CO_2 laser radiation with synthesizer-derived microwave radiation in a CdTe-buffered GaAs stripline electrooptic waveguide modulator. For $NCH-NH_3$, a symmetric top spectrum is observed with a band origin at 1041.7 cm^{-1} , blue-shifted ~91.8 cm^{-1} from the hypothetical inversion-free ν_2 band origin of free NH_3 , which indicates a decrease in the van der Waals zero-point binding energy, D_0 , for the excited state. The observed AB of -14.3 MHz, implying a hydrogen-bond extension, is consistent with this blue shift. The vibrationally excited complex does not predissociate within the ~1 ms transit time between the laser excitation region and the bolometer detector, implying that D_0 is greater than the laser frequency, ~1042 cm^{-1} .

Address of Fraser, Pine, and Suenram: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

*Guest Researcher at NIST. Permanent address: Abteilung für Physikalische Chemie, Universität Ulm, Oberer Eselsberg, D-7900 Ulm, West Germany.

ME8 (3:37)

MICROWAVE AND SUBMILLIMETER SPECTROSCOPY OF Ar-NH_3 STATES CORRELATING WITH

$\text{Ar} + \text{NH}_3$ ($j=1$, $|k|=1$)

E. ZWART, H. LINNARTZ, W. LEO MEERTS, G. T. FRASER, D. D. NELSON, JR., AND W. KLEMPERER

Molecular-beam electric-resonance, electric-resonance optothermal, pulsed-nozzle Fourier-transform, and submillimeter absorption spectroscopy have been used to measure the microwave and submillimeter spectra of Ar-NH_3 for the two Σ and two Π states correlating asymptotically with $\text{Ar} + \text{NH}_3$ ($j=1$, $|k|=1$). For a number of the transitions ^{14}N quadrupole hyperfine structure has been resolved and relative intensity measurements have been made. The two Σ states are found to lie below the two Π states and are separated by approximately the inversion splitting of free NH_3 . For the Π states the NH_3 inversion tunneling is nearly quenched, being only weakly allowed through Coriolis interactions with the nearby Σ states. The strong Coriolis interactions also give rise to a "pure-inversion" $K=0$ type Q-branch with a band origin at ~ 22.7 GHz. All the above are interpreted using a model internal-rotation inversion Hamiltonian, leading to detailed information about the anisotropy of the intermolecular potential.

Address of Zwart, Linnartz, and Meerts: Fysisch Laboratorium, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

Address of Fraser: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

Address of Nelson: Aerodyne Research Corporation, 45 Manning Road, Billerica, MA 01821.

Address of Klemperer: Department of Chemistry, Harvard University, Cambridge, MA 02138.

ME9 (3:54)

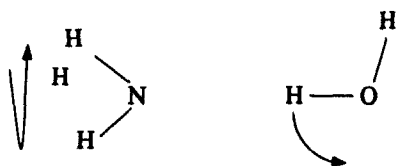
MICROWAVE AND TUNABLE FAR-INFRARED LASER SPECTROSCOPY OF AMMONIA-WATER DIMER

P.A. Stockman; R.E. Bumgarner, S. Suzuki, P.G. Green, and G.A. Blake

Microwave and far-infrared spectra of the $\text{H}_3\text{N-HOH}$ dimer were recorded from 36 to 86 GHz and from 520 to 800 GHz in a planar supersonic jet. The microwave data extended the previous $K=0$ manifold measurements of Herbine and Dyke [1] to higher frequency and also provided a complimentary set of ground state transitions in the $K=1$ manifold. The far-infrared data contained 2 sets of 3 bands, one set shifted from the other by an approximately constant 113 MHz splitting. The bands were assigned to $|m', K' \rangle \leftarrow |m'', K'' \rangle$ transitions $|0, \pm 1 \rangle \leftarrow |0, 0 \rangle$, $|\pm 1, 0 \rangle \leftarrow |\pm 1, \pm 1 \rangle$, and $|\pm 1, \pm 2 \rangle \leftarrow |\pm 1, \pm 1 \rangle$, where m is the NH_3 internal rotation quantum number. The 113 MHz splitting arises from the in-plane water tunnelling motion. From these data were obtained rotational constants and structural parameters. Non-linear least-squares fits to an internal rotor Hamiltonian also provided a limit on the height of the barrier to rotation for the NH_3 monomer.

[1] P. Herbine and T.R. Dyke, J. Chem. Phys. 83, 3768 (1985).

Address: Department of Geology and Planetary Sciences 170-25, California Institute of Technology, Pasadena, CA 91125.



ammonia-water dimer

ME10 (4:11)**THE MICROWAVE SPECTRUM OF BENZENE•SO₂: A NEARLY FREE INTERNAL ROTOR
A. TALEB-BENDIAB, K. W. HILLIG II, AND R. L. KUCZKOWSKI**

The ground internal rotation state ($m = 0$) microwave spectrum of benzene•SO₂ has been reported previously [1]. It was shown that the spectrum is characteristic of an asymmetric top and displays a- and c-type transitions. It was also pointed out that numerous additional transitions occurred in the microwave spectrum of this complex.

Using the Principal Axis Method (PAM) internal rotation Hamiltonian, the $m = 0$ state transitions and the "additional" transitions have been assigned. The existence of a rich spectrum for benzene•SO₂ is due to the internal rotation of benzene about its C₆ axis with a 6-fold potential barrier. The barrier height, V_6 , is 0.3 cm⁻¹. Transitions arising from internal rotation states as high as $m = \pm 5$ were seen with our FTMW spectrometer. The internal rotation microwave spectrum of benzene-d₆•SO₂ was also assigned. Further information on the magnitude of the tilt angle of the benzene plane and the tilt angle of the C₂ axis of SO₂ with respect to the line joining their centers of mass was obtained.

¹A. M. Andrews, M. S. LaBarge, A. Taleb-Bendiab, K. W. Hillig II and R. L. Kuczkowski, TF5, 45th Symposium on Molecular Spectroscopy, Ohio State University (1989). See also: Chem. Phys. Lett. **159**, 559 (1989).

Address: Department of Chemistry, University of Michigan, 930 N. University Ave., Ann Arbor, Michigan 48109, U.S.A.

ME11 (4:28)**THE MICROWAVE SPECTRUM OF TOLUENE•SO₂: A LOW BARRIER INTERNAL ROTOR
A. TALEB-BENDIAB, K. W. HILLIG II, AND R. L. KUCZKOWSKI**

The microwave spectrum of toluene•SO₂ has been observed using the FTMW technique. The spectrum displays a-, b- and c-type transitions. The transitions occur as doublets arising from the internal rotation of the methyl group. The transitions were fit using the Principal Axis Method (PAM) internal rotation Hamiltonian with a 3-fold symmetry potential barrier. The barrier height, V_3 , is 85 cm⁻¹. The internal rotation spectra of toluene-CD₃•SO₂ and toluene-d₈•SO₂ were also assigned. For structural purposes the $m = 0$ transitions of toluene•S¹⁸O₂ and toluene•S¹⁶O¹⁸O were measured. Toluene•SO₂ has no plane of symmetry in its equilibrium geometry. The toluene and SO₂ planes are approximately parallel; the distance, R_{cm} , joining their centers of mass is 3.37 Å. The dipole moment of the complex is 1.87 D.

Address: Department of Chemistry, University of Michigan, 930 N. University Ave., Ann Arbor, Michigan 48109, U.S.A.

ME12 (4:45)

VIBRATIONAL AND ROTATIONAL PROPENSITY RULES FOR THE VIBRATIONAL PREDISSOCIATION OF Ar-CO₂

E.J. BOHAC, MARK D. MARSHALL, AND R.E. MILLER

Vibrational predissociation in Ar-CO₂ has been studied at the state-to-state level in order to determine both the vibrational and rotational propensity rules associated with this process. The technique used in this study involves the direct measurement of the angular distribution of the photofragments using an apparatus based on the optothermal technique. Dissociation is found to proceed via the highest available photofragment vibrational channel. An interesting even/odd rotational propensity is observed, which is consistent with the results of collisionally based calculations for this system.

The dissociation energy is also determined from these experiments, and combined with the results already available in the literature, is used to refine previously reported two dimensional Ar-CO₂ potential energy surfaces. The adjusted potentials which differ from the previous ones primarily in the steepness of the surface with respect to angular displacements from equilibrium, are used to predict the van der Waals stretching frequency and the energy of other excited vibrational states.

Address of Bohac, Marshall and Miller: Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599.

Permanent Address of Marshall: Department of Chemistry, Amherst College, Amherst, MA 01002.

ME13 (5:02)

PERTURBATIONS IN THE 3 μ VIBRATIONAL SPECTRUM OF THE ACETYLENE-CARBON MONOXIDE VAN DER WAALS MOLECULE, HCCH-CO

MARK D. MARSHALL, J.S. MUENTER, AND R.E. MILLER

In the analysis of the 3 μ vibration-rotation spectrum of HCCH-¹²C¹⁸O, several lines showed the effects of a perturbation to the upper state.¹ These included shifts from the expected transition frequency and the appearance of extra, weak features in the spectrum. This perturbation has been found to persist in the analogous spectrum of the HCCH-¹³CO isotopomer suggesting that a combined analysis of the two isotopic species may shed additional light on the nature of the perturbing state or states.

The original spectrum of HCCH-¹²CO has been re-recorded with greater resolution and additional sensitivity. This has allowed a more precise measurement of the additional, weak, perturbation-induced lines in the spectrum.

In addition the spectrum of HCCH-¹³CO has confirmed the previously proposed linear, carbon-bonded structure for the molecule.

1. M.D. Marshall, D.G. Prichard, and J.S. Muentner, *J. Chem. Phys.* **90**, 6049 (1989).

Address of Marshall and Miller: Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599.

Address of Muentner: Department of Chemistry, University of Rochester, Rochester, NY 14627.

Permanent Address of Marshall: Department of Chemistry, Amherst College, Amherst, MA 01002.

Time required: 15 minutes

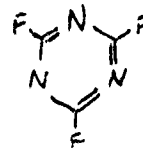
Session in which paper is recommended for presentation: (9) Molecular beam

MF1 (1:30)

SPECTRUM OF THE ν_{11} BAND OF CYANURIC FLUORIDE

P. E. FLEMING AND C. W. MATHEWS

The rotationally resolved spectrum of the ν_{11} band of cyanuric fluoride (out-of-plane ring bending)¹ which is centered near 820 cm^{-1} , was obtained using a Bruker IFS 120HR Fourier Transform spectrometer. The parallel band shows well defined P, Q and R branches and only a very slight degradation to longer wavelengths. Preliminary data at a resolution of 0.01 cm^{-1} yields a lower state rotational constant of $B'' = 0.0656\text{ cm}^{-1}$ based on 116 assigned lines. The K structure is not resolved, however each rotational line shows vibrational satellites consistent with combination bands overlapping the fundamental as has been suggested in the rotational Raman spectrum². Further analysis of the fundamental and combination bands will be presented.



¹J. E. Griffiths and D. E. Irish, *Can. J. Phys.*, **42**, 690 (1964).

²J. Schlupf and A. Weber, *J. Mol. Spectrosc.*, **54**, 10 (1975).

Address: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

MF2 (1:42)

THE BENDING STATES ASSOCIATED WITH THE EXCITED STRETCHING STATES ν_1 , ν_2 , $2\nu_3$ AND $\nu_2 + \nu_3$ OF HCNO

B.P. WINNEWISSER, M. WINNEWISSER AND S. ALBERT

The region $2000\text{--}3600\text{ cm}^{-1}$ in the spectrum of the parent isotopic species of HCNO has been measured with the Bruker IFS 120 HR at Doppler resolution. In addition to the fundamental bands in this region, the spectrum shows a large number of hot bands and combination and difference bands involving the bending modes ν_4 and ν_5 only a few of which were observed in earlier work^{*}.

The line positions have been analyzed, giving information on the bending manifolds in the excited stretching states, which in turn extend our understanding of the interaction between the stretching and bending modes. The interpretation of the line position data is consistent with the intensities observed for the combination and difference bands. With the precision of the spectra we have now obtained, it can be seen that nearly every band identified in this region is at least slightly perturbed. The most important perturbations will be discussed.

^{*}B.P. V. Winnewisser, *J. Mol. Spectrosc.* **40**, 164-176 (1971); E.L. Ferretti and K. Narahari Rao, *J. Mol. Spectrosc.* **51**, 97-106 (1974); E.L. Ferretti, *Dissertation*, The Ohio State University, (1974).

Address of B.P. Winnewisser, M. Winnewisser and S. Albert: Physikalisch-Chemisches Institut, Justus-Liebig-Universität, D-6300 Giessen, Germany.

MF3 (1:59)

ROVIBRATIONAL ANALYSIS OF THE HIGH RESOLUTION FT-IR SPECTRA OF THE C≡N STRETCHING BANDS ν_1 AND ν_2 OF ISOCYANOGEN, CNCN

F. STROH AND M. WINNEWISER

Since our last report* on the high resolution rotational spectrum of isocyanogen, CNCN, we completed measurements of the high resolution FT-IR spectrum of this species between 150 cm^{-1} and 2400 cm^{-1} using the Bruker IFS 120 HR.

The C≡N stretching band systems ν_1 and ν_2 centered around 2302.0 cm^{-1} and 2059.7 cm^{-1} , respectively, were observed with an unapodized resolution of 0.003 cm^{-1} which is just below the Doppler linewidth. We obtained signal to noise ratios of up to 300 and 450 for the lines of the fundamental bands ν_1 and ν_2 , respectively. This made possible the assignment of hot band transitions in both band systems originating from the states with up to 3 quanta of the cis-bending mode ν_5 , the singly excited trans bending mode ν_4 , and the combination state $(\nu_4 \nu_5) = (11)$. Up to now we have assigned around 2500 lines in the two band systems. In the case of the ν_2 fundamental band we expect to identify the transitions of the ^{13}C isotopomers in natural abundance.

We also have assigned around 1000 transitions in the bands due to the trans and cis bending modes ν_4 and ν_5 located at 463.5 cm^{-1} and 194.8 cm^{-1} , respectively. This will allow the determination of the vibrational energy level diagram for the bending states starting from the ground state and the corresponding bending stacks associated with ν_1 and ν_2 . Adjusted spectroscopic constants of an effective hamiltonian will be presented.

*M.C.L. Gerry, F. Stroh and M. Winnewisser, *J. Mol. Spectrosc.* **140**, 147-161 (1990).

Address of F. Stroh and M. Winnewisser: Physikalisch-Chemisches Institut, Justus-Liebig-Universität, D-6300 Giessen, Germany.

MF4 (2:16)

OBSERVATION OF DYNAMIC STARK SPLITTING IN INFRARED-INFRARED DOUBLE RESONANCE IN METHYL FLUORIDE

Quan Song and R. H. Schwendeman

Dynamic Stark splitting (Rabi splitting) has been observed in the $P(5,3)$ transition in the $2\nu_3 \leftarrow \nu_3$ band of $^{13}\text{CH}_3\text{F}$ while pumping the $R(4,3)$ transition in the ν_3 band with 1-5 W of infrared power from a $9\text{P}(32)$ $^{12}\text{C}^{16}\text{O}_2$ laser. The splitting was observed by scanning the probe transition by means of an infrared microwave sideband laser of the Magerl design.¹ The lineshape of the double resonance effect has been fit to good accuracy by means of a least-squares fitting program that solves the density matrix equations for a three-level system followed by integration over the molecular velocity and summation over the spatially-degenerate m states. The effects on the lineshape of changes in pressure and pumping power, of non-parallel pump and probe beams, and of frequency jitter in either of the lasers will be described. A corresponding splitting has also been observed in the $Q(12,9)$ and $R(12,9)$ transitions in the $2\nu_3 \leftarrow \nu_3$ band of $^{12}\text{CH}_3\text{F}$ while pumping the $R(11,9)$ transition in the ν_3 band with the $9\text{P}(22)$ $^{12}\text{C}^{16}\text{O}_2$ laser. No splitting was observed in the $R(12,2)$ transition in the hot band of this molecule while pumping the $Q(12,2)$ transition in the fundamental band with the $9\text{P}(20)$ $^{12}\text{C}^{16}\text{O}_2$ laser. The theoretical reason for the lack of splitting in this double-resonance combination will be discussed. The $R(4,3)$ transition in the ν_3 band of $^{13}\text{CH}_3\text{F}$ has been simultaneously pumped and probed in a two-level double-resonance experiment and the resulting spectrum has been used to obtain a precise value for the offset of the frequency of this transition from the $9\text{P}(32)$ $^{12}\text{C}^{16}\text{O}_2$ laser.

¹G. Magerl, W. Schupita, and E. Bonek, *IEEE J. Quantum Electron.* **QE-18**, 1214-1220 (1982).

Address of Song and Schwendeman: Department of Chemistry, Michigan State University, East Lansing, MI 48824.

MF5 (2:33)

FOREIGN GAS EFFECTS ON COLLISIONAL ENERGY TRANSFER IN METHYL FLUORIDE OBSERVED BY FOUR-LEVEL INFRARED-INFRARED DOUBLE RESONANCE

Quan Song and R. H. Schwendeman

Collisional energy transfer in samples containing 2 mTorr of $^{12}\text{CH}_3\text{F}$ or $^{13}\text{CH}_3\text{F}$ in much higher concentrations of foreign gases such as $^{13}\text{CH}_3\text{F}$ or $^{12}\text{CH}_3\text{F}$, H_2 , He, Ar, or Xe have been studied by the method of four-level infrared-infrared double resonance. In each case a transition in the ν_3 fundamental band was pumped by a CO_2 laser coincidence and the lineshapes of a variety of transitions in the ν_3 fundamental band and the $2\nu_3 \leftarrow \nu_3$ hot band were recorded by scanning an infrared microwave sideband laser of the Magerl design.¹ With methyl fluoride, H_2 , or He as the foreign gas at relatively low pressure (50 mTorr), the lineshapes of the probed transitions consist of a narrow spike plus a Gaussian for pump-probe combinations for which $\Delta k = 3n$ ($n = 0$ or an integer) and only a Gaussian for $\Delta k \neq 3n$, as has been observed in pure $^{13}\text{CH}_3\text{F}$ ² and $^{12}\text{CH}_3\text{F}$.³ With Ar and especially Xe the lineshapes are almost entirely Gaussian, although the $\Delta k = 3n$ transitions are more intense than the $\Delta k \neq 3n$ transitions. With high pressures (1 - 12 Torr) of Ar, the width of the double resonance lineshape is substantially larger than the single resonance lineshape for the same sample and the center frequency of the double resonance undergoes a shift, proportional to pressure, to frequencies corresponding to velocity groups with the opposite sign of the velocity component pumped. The shift in frequency for the double resonance is substantially greater than the shift for the single resonance in the same sample. Collisional energy transfer from $\nu_3 = 1$ to $\nu_6 = 1$ in $^{12}\text{CH}_3\text{F}$ has also been observed in these systems by pumping a transition in the ν_3 band and probing a transition in the $\nu_3 + \nu_6 \leftarrow \nu_6$ band; no transferred spikes have been seen for this vibrational energy transfer. Collisional energy transfer from $\nu_3 = 1$ in $^{13}\text{CH}_3\text{F}$ to $\nu_3 = 1$ and $\nu_6 = 1$ in $^{12}\text{CH}_3\text{F}$ has also been observed

¹G. Magerl, W. Schupita, and E. Bonek, IEEE J. Quantum Electron. **QE-18**, 1214-1220 (1982).

²Y. Matsuo and R. H. Schwendeman, J. Chem. Phys. **91**, 3966-3975 (1989).

³U. Shin, Q. Song, and R. H. Schwendeman, private communication.

Address of Song and Schwendeman: Department of Chemistry, Michigan State University, East Lansing, MI 48824.

MF6 (2:50)

POLARIZATION EFFECTS IN INFRARED-INFRARED DOUBLE RESONANCE IN METHYL FLUORIDE

Uhyon Shin and R. H. Schwendeman

A variety of polarization phenomena have been observed in three-level and four-level infrared-infrared double-resonance experiments in $^{13}\text{CH}_3\text{F}$. For each of these experiments, the $\text{R}(4,3)$ transition in the ν_3 band was pumped by the 9P(32) $^{12}\text{C}^{16}\text{O}_2$ laser while a transition in the ν_3 fundamental band or the $2\nu_3 \leftarrow \nu_3$ hot band was recorded by means of an infrared microwave sideband laser of the Magerl design. For this work, a plane-polarized pump laser beam was converted to circular polarization by passing the beam through a CdTe crystal that was subjected to its quarter-wave electric field by applying 2.1 kV across the crystal. The polarization of the beam could be switched from right to left circular polarization by switching the polarity of the field by means of circuit designed by Martin Rabb at MSU. By directing the circularly-polarized beam through a Fresnel rhomb, the polarization could be switched between horizontal and vertical plane polarization. Thus, double resonance by alignment modulation could be observed by detecting a vertically-polarized probe beam while the pump beam was switched between horizontal and vertical polarization. Similarly, double resonance by orientation modulation could be observed by detecting a circularly-polarized probe beam while switching between right and left circular polarization of the pump beam. By detecting a vertically polarized probe beam through a polarizer oriented at 45° while switching between right and left circular polarization of the pump beam, a dispersion lineshape could be observed. The sign of the dispersion depends on whether the branches of the pump and probe transitions are PP, PR, RP, or RR. The intensity of the dispersion is very much smaller if either or both of the pump or probe beam is a Q-branch transition. The effects of orientation modulation have been observed in four-level double resonance in which the J values of the pump and probe transitions differ by as much as five, which demonstrates that the orientation of the angular momentum vector is not completely randomized by collisions that cause substantial changes in the angular momentum of the molecules.

Address of Shin and Schwendeman: Department of Chemistry, Michigan State University, East Lansing, MI 48824.

Intermission

MF7 (3:20)

TRANS-BEND (TUNNELING) AND OVERALL ROTATION ENERGY LEVELS FOR (HF)₂ AND ISOTOPOMERS

V. C. EPA, P. C. GOMEZ, and P. R. BUNKER

The trans-bend and overall rotation energy levels for the dimer (HF)₂ and its isotopomers have been obtained using a basis set of trans-bend and K-type rotation eigenstates. These basis states were calculated numerically using a more exact form of the kinetic energy contribution to the potential energy in the semi-rigid bender Hamiltonian than had been used previously¹. Use of alternative coordinate axes systems to improve convergence and accuracy was investigated.

¹ P. R. Bunker, T. Carrington, Jr., P. C. Gomez, M. D. Marshall, M. Kofranek, H. Lischka, and A. Karpfen, *J. Chem. Phys.*, **91**, 5154(1982).

Address of Epa and Bunker: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

Address of Gomez: Departamento de Estructura Atomico-Molecular y Espectroscopia, Universidad Complutense de Madrid, 28040 Madrid, Spain.

MF8 (3:37)

TORSIONAL SPECTRA OF CH₃CH₃ AND CD₃CD₃: INTENSITY ANALYSIS N. MOAZZEN-AHMADI, A.R.W. MCKELLAR, J.W.C. JOHNS, AND I. OZIER

Spectra of gaseous CH₃CH₃ and CD₃CD₃ have been recorded using a modified Bornem spectrometer.

For CD₃CD₃, the region of the torsional fundamental (208 cm⁻¹) was measured at a resolution of 0.016 cm⁻¹ and an absorption path length of 20 m. The gas temperature and pressure were 168 K and 80 Torr, respectively. In addition, the ν₉ fundamental (650 cm⁻¹) was studied at very high resolution (0.0014 cm⁻¹) with a path length of 2 m at a temperature of 133 K and a pressure of 0.6 Torr.

The ground state torsion-rotation parameters were obtained from a combination of (I) a frequency analysis of 442 lower state combination differences in ν₉ band and its associated hot band ν₉ + ν₄ - ν₄ with (II) a frequency/intensity analysis of the P, Q, and R branches of the torsional fundamental and the Q branch of the first torsional overtone. The torsional dipole moments μ₁ and μ₁ - μ₁ were determined to be 7.41(74) and -19.9(2.0) μD, respectively.

Similar measurements and analyses were carried out for CH₃CH₃. The torsional dipole moments are: μ₁ = 9.27(93) and μ₁ - μ₁ = -30.81(3) μD.

The experimental values of μ₁ and μ₁ - μ₁ are shown to be in excellent agreement with values calculated from theoretical expressions. The shape of the torsional bands can be reproduced in detail with the model used.

Address of Moazzen-Ahmadi: Department of Physics, University of Lethbridge, Lethbridge, Alberta T1K 3M4, Canada.

Address of Johns and McKellar: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.

Address of Ozier: Department of Physics, University of British Columbia, Vancouver, B.C. V6T 2A6, Canada.

MF9 (3:54)

ROTATIONAL DEPENDENCE OF THE PSEUDO-ROTATION TUNNELING SPLITTING IN PF_5

L. H. COUDERT

New very high-resolution data on phosphorous pentafluoride¹ has prompted a renewed interest in the effects of the Berry pseudorotation on the energy levels of this molecule. Although these effects have already been thoroughly investigated by Dalton,² the interaction of the tunneling motion with the overall rotation of the molecule has not been examined yet.

In the present paper, the non-rigid energy levels of PF_5 are reinvestigated using an IAM-like treatment.³ The energy level pattern is first derived and compared with the one obtained by Dalton.² The interaction of the overall rotation of the molecule with the tunneling motion is afterward investigated. This interaction gives rise to a fast rotational dependence of the tunneling splitting, i.e., a variation of the tunneling pattern with the two symmetric top rotational quantum numbers J and K . Unexpectedly enough, the parameters involved in the characterization of this rotational variation are independent on the geometry of the equilibrium configuration of the molecule and on the intermediate configuration of the tunneling path. These results will be discussed along with the fine structure expected for rovibronic transitions.

¹H. Prinz, W. A. Kreiner, G. Magerl, N. Rohringer and W. Schupita, 45th Symposium on Molecular Spectroscopy, Paper RB3, OSU, (1990).

²B. J. Dalton, J. Chem. Phys. 54, 4745-4762 (1991).

³J. T. Hougen, J. Mol. Spectrosc. 114, 395-426 (1985).

Address: Laboratoire de Physique Moléculaire et Atmosphérique, Tour 13, Université Pierre et Marie Curie et CNRS, 4 Place Jussieu, 75252 Paris Cedex 05, France

MF10 (4:11)

ROVIBRATIONAL HAMILTONIAN FOR TRIATOMIC MOLECULE IN RADAU'S COORDINATES

L. H. COUDERT

Makarewicz¹ has shown that the rovibrational Hamiltonian of a symmetrical triatomic molecule takes a simple form when expressed in terms of Radau's coordinates r_1 , r_2 and θ , very similar to the two valence and bond angle coordinates. This Hamiltonian can be further simplified if the two coordinates r_1 and r_2 are frozen. Taking then a simple model potential function, the eigenvalues of this simplified Hamiltonian can be determined exactly for each K value.²

In this paper a trial rovibrational Hamiltonian for triatomic molecules has been derived starting from the one proposed by Makarewicz.² However, $\Delta K > 0$ matrix elements arising from the rotational Hamiltonian were treated rigorously and phenomenological distortion-like parameters were introduced. The Hamiltonian thereby obtained can account for the rotational levels up to $J = 15$ of H_2O in its ground vibrational state³ with an R.M.S. deviation of $4.9 \times 10^{-3} \text{ cm}^{-1}$, using 30 parameters. In the first excited vibrational state $v_2 = 1$ of the same molecule,⁴ the rotational levels up to $J = 9$ are reproduced with an R.M.S. deviation of $1.4 \times 10^{-3} \text{ cm}^{-1}$, using 22 parameters. These results will be discussed and we hope to be able to achieve a better understanding of the four-fold clustering.

¹J. Makarewicz, J. Phys. B: At. Mol. Phys. 21, 1803-1819 (1988).

²J. Makarewicz, J. Phys. B: At. Mol. Phys. 21, 3633-3651 (1988).

³J.-M. Flaud, C. Camy-Peyret and J. P. Maillard, Mol. Phys. 32, 499-521 (1976).

⁴C. Camy-Peyret, J.-M. Flaud, J. P. Maillard and G. Guelachvili, Mol. Phys. 33, 1641-1650 (1977).

Address: Laboratoire de Physique Moléculaire et Atmosphérique, Tour 13, Université Pierre et Marie Curie et CNRS, 4 Place Jussieu, 75252 Paris Cedex 05, France

MF11 (4:28)

VIBRATIONAL SPECTRA, RING-PUCKERING POTENTIAL ENERGY FUNCTION, AND CONFORMATION OF 1,3-DISILACYCLOPENT-4-ENE

LLOYD F. COLEGROVE and JAAN LAANE

1,3-Disilacyclopent-4-ene has been synthesized and its far-infrared, mid-infrared, and Raman spectra have been analyzed. From the far-infrared data of the molecule in the vapor phase, which shows a series of ten bands between 48 and 85 cm^{-1} , the ring-puckering potential energy surface was determined to be $V(\text{cm}^{-1}) = 1.48 \times 10^5 x^4 + 0.30 \times 10^4 x^2$, where x is the ring-puckering coordinate in Angstroms. This shows the molecule to be planar but to be not nearly as rigid as silacyclopent-2-ene.¹ Other features in the infrared, Raman, and nmr spectra confirm that the interactions between the silicon atoms and the carbon-carbon double bond, while present, are reduced relative to silacyclopent-2-ene.

¹ M. B. Kelly and J. Laane, *J. Chem. Phys.*, **92**, 4056 (1988).

Address of authors: Department of Chemistry, Texas A&M University, College Station, Texas 77843.

MF12 (4:40)

l-TYPE RESONANCE IN THE ν_5 BENDING MODE REGION OF C_2H_2 AT 14μ

MARK WEBER, W.C. MAGUIRE, J.J. HILLMANN, AND W.E. BLASS

Using interferometric spectra obtained on the McMath Solar Telescope FTS spectrometer in double pass configuration (0.0025cm^{-1} resolution), improved rotation-vibration molecular parameters of acetylene in the ν_5 region were determined as compared to Refs. (1). The frequency analysis of one and two quantum hotbands involved the states of ν_5 , $2\nu_5$, $\nu_4+\nu_5$, $3\nu_5$, $2\nu_4+\nu_5$, and $\nu_4+2\nu_5$.

The least square fit was based on the numerical diagonalization of the hamiltonian using the Hellman-Feynman theorem which permits the calculation of the effective dipole moment (2,3). FTS data as well as tunable diode laser spectra recorded at the University of Tennessee clearly indicate the dominant *l*-resonance effect upon the hotband intensities; experimental intensities agree well with the predicted values.

(1) J. Hietanen and J. Kauppinen, *Molec. Phys.*, **42**, 411 (1981); J. Hietanen, *Mol. Phys.*, **49**, 1029 (1983).

(2) R.B. Wattson and L.S. Rothman, *J.Mol.Spectr.*, **119**, 83 (1986).

(3) W.F. Rowe and E.B. Wilson, *J.Mol.Spectr.*, **56**, 163 (1975).

Address of Weber and Blass: Molecular Spectroscopy Laboratory, Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996-1200

Address of Maguire and Hillmann: Goddard Space Flight Center, Code 693, Greenbelt, Maryland 20771

MF13 (4:57)**PERPENDICULAR BANDS OF CYCLOPROPANE IN THE 3.5 μm REGION****D. W. MERDES, J. PLÍVA, AND A. S. PINE**

The spectrum of the cyclopropane molecule was measured in the region 2898.5 to 3157.3 cm^{-1} with Doppler-limited resolution using a difference frequency laser spectrometer. Deconvolution was used to further enhance the effective resolution in the main part of the highly perturbed spectrum. The region below $\sim 3060 \text{ cm}^{-1}$ contains perpendicular bands, including the ν_8 fundamental of species E' in close anharmonic resonance with the E' component of the state $\nu_7+\nu_9+\nu_{14}$ and with other E' states, and the $\nu_2+\nu_9$ band which borrows its intensity from ν_8 via Fermi resonance. The $\nu_2+\nu_9$ E' state is also perturbed by anharmonic interactions with additional E' states.

A comprehensive analysis of this complex system of perpendicular bands based on a Hamiltonian model of the main interactions yielded much improved spectroscopic constants for the ν_8 fundamental, for the $\nu_2+\nu_9$ combination and for the newly observed $\nu_7+\nu_9+\nu_{14}$ state, as well as information on seven tentatively identified perturbing states.

Address of Merdes: Applied Research Laboratory, The Pennsylvania State University, PO Box 30, State College, Pennsylvania 16804.

Address of Plíva: Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802.

Address of Pine: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899.

MG1 (1:30)

MATRIX REACTIONS OF BORON ATOMS WITH OXYGEN MOLECULES. INFRARED SPECTRA OF SEVERAL BORON-OXYGEN SPECIES

T. R. Burkholder and L. Andrews

Boron atoms from YAG laser ablation of the solid have been codeposited with Ar/O₂ samples on a 12K salt window. The product infrared spectrum was dominated by 3 strong ¹¹B isotopic bands at 1299.3, 1282.9 and 1274.6 cm⁻¹ with ¹⁰B counterparts at 1347.6, 1330.7 and 1322.2 cm⁻¹. Oxygen isotopic substitution (¹⁶O¹⁸O and ¹⁸O₂) confirms the linear BO₂ assignment of these strong bands. A sharp medium intensity band at 1854.7 has appropriate isotopic ratios for BO, which exhibits an 1862 cm⁻¹ gas phase fundamental. A sharp 1931.0 cm⁻¹ band shows isotopic ratios appropriate for another linear BO₂ species; correlation with spectra of BO₂⁻ in alkali halide lattices confirms this assignment. A weak 1898.9 cm⁻¹ band grows on annealing and shows isotopic ratios for a BO stretching mode and isotopic splittings for 2 equivalent B and O atoms, which confirms assignment to B₂O₂. Weak 2062, 2048 and 2017 cm⁻¹ bands grow markedly on annealing and show isotope shifts appropriate for a terminal -BO group interacting with one other oxygen; these bands are assigned to B₂O₃ in agreement with the Weltner and White groups. The present experiments demonstrate that new boron-containing molecular species can be formed by matrix reactions of boron atoms and suitable molecules. These studies show that charged species can also be produced by pulsed laser ablation.

Address of Burkholder and Andrews: Department of Chemistry, University of Virginia, Charlottesville, VA 22901

MG2 (1:47)

MATRIX REACTIONS OF SULFUR ATOMS AND FLUORINE. INFRARED SPECTRA OF SF, SF₂ AND SF₃ IN SOLID ARGON.

P. Hassanzadeh and L. Andrews

Sulfur vapor diluted with argon was passed through a microwave discharge and codeposited with argon-fluorine samples onto a CsI window at 12K. Variation of fluorine and sulfur concentrations over a wide range and sulfur-34 isotopic substitution provided a basis for identification of the SF, SF₂ and SF₃ transient species. The diatomic SF radical showed matrix site absorptions at 818.8 and 822.0 cm⁻¹ for ³²S¹⁹F and 809.9 and 813.1 cm⁻¹ for ³⁴S¹⁹F. A similar site splitting was also observed for both symmetric and antisymmetric stretching vibrations of SF₂ at 832.5, 829.5 and 805.0, 804.6, 802.1 cm⁻¹, respectively. The SF₃ radical revealed symmetric equatorial and antisymmetric axial stretching vibrations at 843.8 and 681.8 cm⁻¹, respectively. Sample annealing increased weak absorptions due to the higher fluoride species in the series including SF₄ and SF₆.

Address of Hassanzadeh and Andrews: Department of Chemistry, University of Virginia, Charlottesville, VA 22901

MG3 (2:04)

INFRARED SPECTRA OF NEW NITROGEN-SULFUR SPECIES IN ARGON MATRICES.
P. Hassanzadeh and L. Andrews

New nitrogen-sulfur species were produced by the addition of sulfur vapor into an argon/nitrogen microwave discharge generated within a constricted orifice discharge tube, and the reaction products were trapped in argon matrices at 12K. Nitrogen-15 and sulfur-34 isotopic substitutions, concentration variation, photolysis and changes upon annealing provided a basis for identification and characterization of the new products. A relatively weak absorption at 1209.4 cm^{-1} is assigned to the diatomic NS radical. An intense absorption at 1225.2 cm^{-1} , which showed a triplet absorption with mixed sulfur isotopes and a doublet with mixed nitrogen isotopes, is assigned to the antisymmetric stretching vibration of SNS. An absorption band at 2040.2 cm^{-1} , which showed quartet and doublet patterns with mixed nitrogen and mixed sulfur isotopes, respectively, is assigned to the nitrogen-nitrogen stretching fundamental of N_2S . Bond lengths, bond angles and infrared absorptions predicted from ab initio calculations will also be presented.

Address of Hassanzadeh and Andrews: Department of Chemistry, University of Virginia, Charlottesville, VA 22901

MG4 (2:21)

THE VIBRATIONAL SPECTRA OF CO^+ , C_2O_2^+ , AND C_2O_2^- ISOLATED IN SOLID NEON
 WARREN E. THOMPSON* AND MARILYN E. JACOX

When a $\text{Ne}:\text{CO} = 100$ mixture is codeposited at approximately 5 K with a beam of neon atoms that have been excited in a microwave discharge, several new infrared absorptions appear in the resulting sample deposit. The analysis of detailed isotopic substitution experiments, which supports the assignment of these absorptions to CO^+ , trans-OCO^+ , and trans-OCO^- , will be presented. This analysis has also permitted determination of the CO-stretching force constants of the dimer cation and anion and has yielded a preliminary estimate of the valence angles for trans-OCO^- .

* Guest Researcher at the National Institute of Standards and Technology.

Address of Thompson: National Science Foundation, Washington, D. C. 20550.
Address of Jacox: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899.

MG5 (2:38)

THE MID- AND NEAR-INFRARED SPECTRA OF HC_2 ISOLATED IN SOLID ARGON AND NEON
DANIEL FORNEY* AND MARILYN E. JACOX

Observations of the mid- and near-infrared spectra of HC_2 isolated in solid neon will be compared with earlier observations of this species isolated in solid argon, as well as with studies of individual gas-phase bands. Further consideration of the carbon-13 and deuterium isotopic shifts of HC_2 in the matrix environment aids in the assignment of several combination bands of this species in the mid-infrared.

* Guest Researcher.

Address: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899.

Intermission

MG6 (3:05)

MATRIX ISOLATION STUDIES OF CHEMICAL VAPOR DEPOSITION: THE $(\text{CH}_3)_3\text{Ga}/\text{AsH}_3$ and $(\text{CH}_3)_3\text{Ga}/\text{PH}_3$ SYSTEMS

Elizabeth A. Piocos and Bruce S. Ault

Lewis acid-base concept predicts the initial formation of a 1:1 molecular adduct between trimethylgallium and arsine, which are gaseous precursors for the chemical vapor deposition of the semiconductor gallium arsenide. Isolation and characterization of this $(\text{CH}_3)_3\text{Ga}\cdot\text{AsH}_3$ adduct for the first time using infrared matrix isolation technique showed that it has an effective symmetry of C_{3v} . The corresponding adduct of phosphine with trimethylgallium has also been isolated and characterized using this technique. In addition, results of gas-phase studies indicate that both adducts may exist in the gas phase. Subsequent 193 nm photolysis of the $(\text{CH}_3)_3\text{Ga}\cdot\text{AsH}_3$ adduct shows that an eliminated methyl radical abstracts a hydrogen to form methane and probably $(\text{CH}_3)_2\text{Ga}\cdot\text{AsH}_2$. The photolysis of $(\text{CH}_3)_3\text{Ga}$ at 193 nm has also been studied and results strongly indicate the production of dimethylgallium and methyl radicals.

Address of Piocos and Ault: Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172.

MG7 (3:22)

INFRARED MATRIX ISOLATION STUDY OF THE REACTION OF B_2H_6 WITH NH_3 AND THE METHYLAMINES.

John D. Carpenter and Bruce S. Ault

The reaction products arising from the pyrolysis of mixtures of B_2H_6 with NH_3 and the methylamines have been isolated and characterized in argon matrices at 14 K. For all three methylamines, the 1:1 adduct $\text{H}_3\text{B}\cdot\text{NH}_x(\text{CH}_3)_y$ ($x+y=3$) was isolated. The 1:1 adduct of B_2H_6 and NH_3 is probably formed but undergoes rapid H_2 elimination to give aminoborane, $\text{H}_2\text{B}=\text{NH}_2$. All 11 infrared active fundamentals of aminoborane were identified including the two lowest fundamentals not previously reported. In addition, the H_2 elimination products were isolated when mono- and dimethylamine were used. $\text{H}_2\text{B}=\text{N}(\text{H})\text{CH}_3$ was also isolated and characterized for the first time. The mechanism of formation of these products from the precursors will be discussed along with experiments currently in progress.

Address of Carpenter and Ault: Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172.

MG8 (3:39)

SPECTROSCOPY OF LOW TEMPERATURE MATRIX ISOLATED NX_2 RADICALS

JULANNA V. GILBERT

Studies of the kinetics of hydrogen atom reactions with NCl_3 and with NFCl_2 performed in our laboratory demonstrated the production of excited state nitrenes in these systems.* The time profiles of the NX emissions are consistent with a two step mechanism involving the formation of NX_2 and NXY intermediates ($\text{X}, \text{Y} = \text{halogens}$), a class of radicals for which there is almost no spectroscopic information available in the literature. Investigations of the spectroscopy of low temperature matrix isolated NX_2 and NXY radicals, prepared by reacting fluorine atoms with the corresponding NX_3 (or NX_2Y) before deposition, are reported.

* Exton, D.B., Gilbert, J.V., Coombe, R.D., J. Phys. Chem., in press.

Address: Department of Chemistry, University of Denver, Denver, Colorado 80208.

MG9 (3:56)

CHARACTERIZATION OF TRAPPING SITES IN RELAXED RARE GAS MATRICES USING MONTE-CARLO SIMULATIONS OF INFRARED MATRIX SHIFTS

Mark R. Davies and Robert J. Le Roy

When a chromophore is trapped inside a rare gas matrix, its characteristic vibrational frequencies are displaced from those of the free molecule. The resulting shifted infrared spectrum depends on the temperature and the nature of the vacancy site occupied by the chromophore. Application of Monte-Carlo averaging techniques to a realistic model for the chromophore-matrix interaction and a means of estimating the frequency shifts, allows us to examine the effect of the size and shape of the trapping site on the predicted spectrum.

In previous work, we examined the effect on the spectrum of placing the chromophore in vacancies of different sizes in a *rigid* lattice. The present study also allows layers of lattice atoms surrounding the chromophore to thermally relax. In general, the shape and nature of the spectrum is dependent on the size and shape of the vacancy, and on the degree of relaxation of the surrounding lattice atoms. This paper will describe our application of this approach to the case of SF₆ molecules in Ar matrices.

Address: Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L3G1, Canada.

MG10 (4:13)

OBSERVATION OF A C≡C STRETCHING FUNDAMENTAL FOR C₆H IN SOLID Ar

T.J. DOYLE, L.N. SHEN, AND W.R.M. GRAHAM

A vibration of the C₆H (hexatriynyl) radical has been identified for the first time at 1953.4 cm⁻¹ in the Fourier transform infrared spectrum of the vacuum ultraviolet photolysis products of acetylene and 1,3-butadiene trapped in Ar at 10 K. The spectra for various D and ¹³C isotopomers of C₆H produced from isotopically substituted precursors have been observed. The complex, overlapping spectra resulting from partial ¹³C substitutions have been fitted using force constant adjustment calculations, and confirm the assignment of the new band as a C≡C stretching fundamental of C₆H, for which a rotational spectrum has been observed in a stellar atmosphere¹ and in the laboratory².

¹H. Suzuki, M. Ohishi, N. Kaifu, S. Saito, and K. Kawaguchi, Publ. Astron. Soc. Japan, **38**, 911 (1986).

²J.C. Pearson, C.A. Gottlieb, D.R. Woodward, and P. Thaddeus, Astron. Astrophys. **189**, L1 (1987).

Address of Doyle and Graham: Department of Physics, Texas Christian University, Fort Worth, Texas, 76129.

Address of Shen: Chemical Engineering, Box 2159, Yale University, New Haven, Connecticut, 06520.

MG11 (4:30)

FT VIBRATIONAL SPECTROSCOPY OF Si_2C IN SOLID ARGON¹

J.D. PRESILLA-MÁRQUEZ, C.M.L. RITTBY, AND W.R.M. GRAHAM

A Fourier transform study of the vibrational spectrum of Si_2C produced by quenching the products of the vaporization of carbon/silicon mixtures in Ar at 13 K has confirmed a previously observed band at 1188.4 cm^{-1} as the $\nu_3''(b_2)$ antisymmetric Si-C stretching mode, and led to the identification of a new vibration at 839.5 cm^{-1} as the $\nu_1''(a_1)$ symmetric Si-Si stretching mode. The $\nu_2''(a_1)$ bending mode was not observed. These results are confirmed by ^{13}C , ^{29}Si , and ^{30}Si isotopic data and are in excellent agreement with the predictions of second order perturbation theory (MBPT2/6-311G(2d)) calculations carried out in conjunction with this work. Force constant adjustment calculations based on these assignments confirm the ground state geometry as a floppy bent symmetrical structure.

¹Work supported by the Welch Foundation (Grant P-0786) and the W.M. Keck Foundation.

Address of Presilla-Márquez, Rittby, and Graham: Department of Physics, Box 32915, Texas Christian University, Fort Worth, Tx 76129.

MG12 (4:47)

DIATOMIC MOLECULES FORMED BY Mo AND W WITH Cu, Ag, AND Au Y. M. HAMRICK, R. J. VAN ZEE, AND W. WELTNER, JR.

The ground states of MoCu , MoAg , MoAu , WCu , WAg , and WAu were determined to be $^6\Sigma$ with zero-field splitting parameters $D > 2\text{ cm}^{-1}$. Hyperfine splittings and nuclear quadrupole coupling constants (in molecules containing Au) were determined. Bonding and electron spin distribution will be discussed and related to earlier studies of the corresponding Cr diatomics.¹

¹ C. A. Baumann, R. J. Van Zee, and W. Weltner, Jr., J. Chem. Phys. 79, 5272 (1983).

Address of Hamrick, Van Zee, and Weltner: Department of Chemistry, University of Florida, Gainesville, FL 32611-2046.

MG13 (5:04)

THE GROUND STATE OF THE B_2 MOLECULE Y. M. HAMRICK, R. J. VAN ZEE, AND W. WELTNER, JR.

The electron spin resonance spectra of $^{10}\text{B}_2$ in neon, argon, and krypton matrices at 4 K are essentially the same and indicate that the molecule has $D_{\infty h}$ symmetry and a 2A_1 ground state. This is in agreement with theoretical calculations¹. The observed spectra and derived magnetic parameters will be discussed.

¹ R. Hernandez and J. Simons, J. Chem. Phys. 94, 2961 (1991) and references given there.

Address of Hamrick, Van Zee, and Weltner: Department of Chemistry, University of Florida, Gainesville, FL 32611-2046

TA1 (8:30)

HIGH SENSITIVE LASER SPECTROSCOPY OF HIGHLY EXCITED MOLECULAR STATES

Invited Paper30 min.

L.N. SIN, TSA, Institute of Atmospheric Optics, SB USSR Academy of Science,
Tomsk, 634055, USSR.

TA2 (9:02)

INTERFACING A 4 METER BASE LENGTH MULTIPASS CELL WITH THE BRUKER FTIR: (0,3,1) AND (1,1,1) BANDS OF D₂O. P.S. ORMSBY, K. NARAHARI RAO, M. WINNEWISSER, AND B.P. WINNEWISSER.

The transfer optics system required to couple a four meter multipass cell to the Bruker Fourier transform spectrometer has been designed. A usable optical path length of approximately 300 meters was easily attained with this system. Low pressure, long path measurements were made in the (0,3,1) and (1,1,1) bands of D₂O in the 1.5 μ m region. Line positions and line assignments, molecular constants, and pressure broadening coefficients have been determined.

Address of Ormsby and Rao: Department of Physics, The Ohio State University, Columbus, Ohio, 43210.

Address of Winnewissers: Physikalisch-Chemisches Institut, Der Justus-Liebig Universität, Giessen, Germany, D6300.

TA3 (9:18)

IR SPECTROSCOPY WITH A DOUBLE MODULATION SIDEBAND TECHNIQUE

W.A. KREINER, L. JÖRISSEN, W. HÖHE, M. LOËTE

We have applied both microwave and radio frequency modulation to CO₂ laser lines using only one CdTe modulator. As a result, a grid of closely spaced ($\Delta\nu \approx 1$ MHz) and tunable infrared frequencies is generated. This technique was used to perform infrared-infrared double resonance experiments on the molecules ²⁸SiH₄ and ²⁸SiF₄ and to observe the Stark splitting due to extremely small dipole moments. As a preliminary result we obtained values for several dipole moment parameters which agree with measurements performed with other techniques.

Address of Kreiner, Jörisson, and Höhe: Abteilung Physikalische Chemie, Universität Ulm, Einsteinallee 11, D-7900 Ulm, Germany.

Address of Loëte: Laboratoire de Spectronomie Moléculaire et Instrumentation Laser, 6, Bd. Gabriel, F-21 000 Dijon, France.

TA4 (9:34)

High Resolution Fourier Transform Spectroscopy in a Supersonic Expansion
Richard Dissly, R.E. Bumgarner, G.A. Blake and H.M. Pickett

A supersonic molecular beam has been coupled to a Bruker 120 Fourier transform spectrometer having an ultimate resolution of 0.0015cm^{-1} . The chamber is pumped with a Balzers model DIF-320 (12 inch) diffusion pump backed by an Alcatel model 2063C mechanical pump resulting in a net pumping speed of about 5000 l/s at 10^{-4} Torr. The system is equipped with a heated nozzle source for studies of slightly volatile species. Preliminary work with this setup will be described.

Address of Dissly, Bumgarner and Blake: Division of Geological and Planetary Sciences, 170-25 Caltech, Pasadena, CA 91125.

Address of Pickett: Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, CA 91109.

TA5 (9:50)

THE HIGH RESOLUTION EMISSION SPECTRUM OF GASEOUS LiF.

H.G. Hedderich, C.I. Frum, R. Engleman, Jr., and P.F. Bernath

The high resolution infrared spectrum of LiF has been measured in emission with the McMath Fourier transform interferometer at Kitt Peak. 800 lines with $v=1\rightarrow 0$ to $v=8\rightarrow 7$ of the main isotopomer ^7LiF and 250 lines with $v=1\rightarrow 0$ to $v=3\rightarrow 2$ of the minor isotopomer ^6LiF were observed. These ro-vibrational transitions and pure rotational transitions from the literature¹ were fit to a set of Dunham coefficients Y_{ij} and a set of mass-reduced Dunham coefficients U_{ij} . The infrared spectrum of LiF was found "accidentally" during an attempt to measure the infrared spectrum of MgF_2 .

¹E.F. Pearson and W. Gordy, *Phys. Rev.*, **177**, 52-58 (1969)

Address of Hedderich and Bernath: University of Waterloo, Department of Chemistry, Centre for Molecular Beam and Laser Chemistry, Waterloo, Ontario, Canada N2L 3G1.

Address of Frum and Engleman: Department of Chemistry, University of Arizona, Tucson, Arizona 85721, U.S.A.

TA6 (10:01)

HIGH RESOLUTION INFRARED SPECTROSCOPIC DIAGNOSTICS OF AC GLOW DISCHARGES

S. S. LEE, C. M. GABRYS, M. ROSSLEIN, AND T. OKA

The velocity modulation lineshapes and velocities of ions in the positive column of AC glow discharges have been studied with difference frequency and diode lasers. The lineshape study was based on the mathematical model proposed by Solka *et al*¹. The 2f signals of a variety of ions were used to examine this model. The evolution of lineshape with phase is the result of ion lifetime, modulation frequency, and the effective duration of the discharge current. From the splitting of the 2f signal, with known effective electric field in the positive column, it is possible to derive ion mobility directly. The axial and radial electric fields (or ion velocities) in the positive column were found to be of the same magnitude, which is in agreement with the result reported by Ganguly and Garscadden.²

¹H. Solka, W. Zimmermann, D. Reinert, A. Stahn, A. Dax, and W. Urban, *Appl. Phys. B* **48**, 235 (1989)

²B. N. Ganguly and A. Garscadden, *Phys. Rev. A* **32**, 2544 (1985)

Address of Lee, Gabrys, Rosslein, and Oka: Department of Chemistry and Department of Astronomy and Astrophysics, the University of Chicago, Chicago, IL 60637.

Intermission

TA7 (10:30)

OBSERVATION OF THE $3\nu_2 \leftarrow 0$ OVERTONE BAND OF H_3^+

S. S. LEE, B. F. VENTRUDO, D. T. CASSIDY, T. OKA, S. MILLER, AND J. TENNYSON

We report the observation the second overtone band¹ ($3\nu_2(l=1) \leftarrow 0$) of H_3^+ using a 1.45 μm InGaAsP near infrared diode laser with the short external cavity mode control technique developed at McMaster University.² H_3^+ was generated using 1.5 Torr of H_2 with or without 4 ~ 5 Torr of He in a liquid- N_2 cooled multiple-inlet-multiple-outlet discharge cell. The H_3^+ signal was detected with velocity modulation or ion concentration modulation in an AC glow discharge. Altogether four lines have been observed in the region of 6860 ~ 6925 cm^{-1} . The positions of the lines were determined using a wavemeter calibrated with H_2O reference lines. The assignment of the transitions is based on Miller and Tennyson's first principles calculation³ and on observed temperature dependence of the relative intensities. Extended search of other transitions is being conducted. It is our hope that this observation may lead to detection of H_3^+ in higher vibrational states in Jupiter and other astronomical objects, and that it may also help in the assignment of the laboratory FTIR emission spectrum of hydrogen plasma.

¹S. S. Lee, B. F. Ventrudo, D. T. Cassidy, T. Oka, S. Miller, and J. Tennyson, *J. Mol. Spec.* **145**, 222 (1991).

²D. T. Cassidy, *Appl. Opt.* **27**, 610 (1988).

³S. Miller and J. Tennyson, *private communication*.

Address of Lee and Oka: Department of Chemistry and Department of Astronomy and Astrophysics, the University of Chicago, Chicago, IL 60637.

Address of Ventrudo and Cassidy: Department of Engineering Physics, McMaster University, Hamilton, Ontario, Canada L8S 4M1.

Address of Miller and Tennyson: Department of Physics and Astronomy, University College London, Gower Street, London, United Kingdom WC1E 6BT

TA8 (10:46)

OBSERVATION OF FORBIDDEN TRANSITIONS OF H_3^+

L.-W. XU, M. RÖSSLEIN, C. GABRYS AND T. OKA

Due to the large anharmonicity and vibration-rotation interactions in the H_3^+ , the IR forbidden transitions $\nu_1 + \nu_2 \leftarrow \nu_2$ and $\nu_1 \leftarrow 0$ can borrow intensity from the allowed $2\nu_2 (l=2) \leftarrow \nu_2$ and $\nu_2 \leftarrow 0$ bands. Using the *ab initio* calculation¹ as a guide, we searched for these transitions using the difference frequency laser system in the region from 2840 cm^{-1} to 3280 cm^{-1} . H_3^+ was produced in a liquid nitrogen cooled AC glow discharge of H_2 and He mixtures. About 170 new lines have been observed, and the analysis is under way. Up to now, 12 lines have been assigned to the band $\nu_1 + \nu_2 \leftarrow \nu_2$; and 2 lines to $\nu_1 \leftarrow 0$. During this process, we have also assigned many new transitions for the other bands.

The forbidden transitions of H_3^+ is of special interest for astrophysics since it is an important mechanism to cool down the excited H_3^+ in the space. It also gives absolute rovibrational energy values for the ν_1 and the $\nu_1 + \nu_2$ states.

¹S. Miller, J. Tennyson and B. T. Sutcliffe, *J. Mol. Spectrosc.* **141**, 104-117 (1990).

Addresses of Xu, Rösslein, Gabrys and Oka: Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, IL 60637 - 1403.

TA9 (11:02)

INFRARED SPECTROSCOPY AND EQUILIBRIUM STRUCTURE OF H_2O^+

T.R. HUET, C.J. PURSELL, W.C. HO, B.M. DINELLI and T. OKA

The results of our recent characterization of the ν_1 state of H_2O^+ (X^2B_1) combined with these on ν_2 [1] and ν_3 [2] allowed us to determine the equilibrium structure and the harmonic and cubic potential constants of this ion. As previously reported [3], experimental conditions have been found to favor the formation of the H_2O^+ ion over the more abundant H_3O^+ ion. The spectra have been recorded in a pure He discharge owing to a small water impurity in the He tank. A color center laser spectrometer along with velocity modulation detection was used to record spectra of H_2O^+ produced in a AC glow discharge between 3100 and 3600 cm^{-1} .

The ν_1 band of H_2O^+ has been assigned up to $J', K_a' = 9,3$ and the previous analysis of the ν_3 band [2] has been extended up to $J', K_a' = 8,6$. The ν_1 and ν_3 bands have been fitted together taking into account the Coriolis interaction. Molecular constants have been obtained for ν_1 and have been improved in the case of ν_3 and the ground state. Our actual attempts to identify the $(\nu_2+\nu_3) - \nu_2$ hot band will be also reported.

1. H. Lew, Can. J. Phys. **54**, 2028-49 (1976) ; P.R. Brown et al., J. Chem. Phys. **91**, 3384-91 (1989).
2. B.M. Dinelli, M. Crofton and T. Oka, J. Mol. Spectrosc. **127**, 1-11 (1988).
3. Abstract RA10 of the 44th Symposium on Molecular Spectroscopy, The Ohio State University (1989).

Address of Huet and Oka: Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago ; Chicago, Illinois 60637.

Address of Pursell : Department of Chemistry, Indiana University ; Bloomington, Indiana 47405.

Address of Ho : Department of Physics, University of British Columbia ; Vancouver, B.C. V6T 2A6 (Canada).

Address of Dinelli : Istituto di Spettroscopia Molecolare, Via de'Castagnoli 1 ; 40126 Bologna (Italy).

TA10 (11:18)

INFRARED STUDIES OF THE ν_4 BAND OF CH_2D^+

M. ROSSLEIN, M.-F. JAGOD, C. GABRYS, and T. OKA

During our studies of the infrared spectra of $\text{HCCD}^+{}^1$ we have also scanned parts of the ν_4 fundamental vibrational rotational band of CH_2D^+ . The monodeuterated methyl cation is produced in a liquid nitrogen-cooled AC-glow discharge with a gas mixture of $\text{He:H}_2\text{:CD}_4\text{:CH}_4$ (700:4:4:1 or 7000:10:12:1) with a total pressure of ≈ 7 torr. The spectra of the species were recorded using a difference frequency spectrometer and velocity modulation. The detailed analysis of the ν_4 vibrational rotational band is underway.

The monodeuterated methyl cation is of special interest for radioastronomical search of the acetylene ion in interstellar space and planetary ionospheres because of the presence of an effective permanent dipole moment. The methyl cation is a very important intermediate in the formation of interstellar molecules.

¹M.-F. Jagod, M. Rösslein, C. Gabrys, B. D. Rehfuss, F. Scappini, M. W. Crofton and T. Oka, *J. Chem Phys* to be sub. (1991)

Address: Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, IL 60637-1403

TA11 (11:34)

INFRARED SPECTROSCOPIC STUDY OF THE QUASILINEARITY OF NH_2^+ ION

Y. KABBADI, T.R. HUET, S.E. CHOI AND T. OKA

In a previous work ⁽¹⁾ indirect evidence from the spectrum of the ν_3 band of NH_2^+ in the X^3B_1 ground electronic state has suggested that this ion is quasilinear. Analogous conclusion is obtained from ab initio calculations ⁽²⁾.

An important parameter for quantifying the quasilinear nature of NH_2^+ is the rotational constant A.

More spectroscopic work and analysis on the quasilinearity of NH_2^+ will be reported. These concern :

- 1) our attempts to identify some unassigned rovibrational lines in the $3\ \mu$ region and to observe the ν_2 band.
- 2) the recent rovibrational ab initio calculations.

1. M. Okumura, B.D. Rehfuss, B.M. Dinelli, M.G. Bawendi and T. Oka : J. Chem. Phys., **90**, 5918 (1989)

2. P. Jensen, P.R. Bunker and A.D. McLean : Chem. Phys. Lett., **141**, 53 (1987)

Address of Kabbadi, Huet and Oka : Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois 60637.

Address of Choi : The James Frank Institute, The University of Chicago, Chicago, Illinois 60637

TA12 (11:50)

NEW OBSERVATIONS OF ELECTRONIC TRANSITIONS OF H_3 AND D_3 IN THE INFRARED AND VISIBLE REGIONS

W. A. MAJEWSKI, A. R. W. MCKELLAR, D. SADOVSKII, M. VERVLOET and J. K. G. WATSON.

Extensive spectra of the H_3 and D_3 molecules have been observed in the infrared and visible regions using two different sources: one is a quartz nozzle of Droege-Engelking type¹, in which a mixture of H_2 or D_2 with Ar was subjected to a high-voltage discharge; and the other is the hollow-cathode discharge source using pure H_2 or D_2 , described in previous Symposia². In the nozzle source the Ar apparently quenches the normal H_2 or D_2 emission, and the lines of H_3 or D_3 can readily be distinguished from those of atomic Ar, or ArH or ArD by their greater Doppler width. In the hollow-cathode source, the H_3 or D_3 lines are distinguished from those of H_2 or D_2 by the pressure dependence of their relative intensities. The new spectra will be compared with the original spectra³⁻⁶, which had rather extensive interference in some regions due to H_2 or D_2 lines.

1. A. T. Droege and P. C. Engelking, *Chem. Phys. Lett.* **96**, 316-318 (1983).

2. Papers TE7 (1985), RE5 (1986), WF3 (1987), RA2 (1989), and RF9 (1990).

3. I. Dabrowski and G. Herzberg, *Can. J. Phys.* **58**, 1238-1249 (1980).

4. G. Herzberg and J. K. G. Watson, *Can. J. Phys.* **58**, 1250-1258 (1980).

5. G. Herzberg, H. Lew, J. J. Sloan, and J. K. G. Watson, *Can. J. Phys.* **59**, 428-440 (1981).

6. G. Herzberg, J. T. Hougen, and J. K. G. Watson, *Can. J. Phys.* **60**, 1261-1284 (1982).

Address of Majewski, McKellar, Sadovskii, and Watson: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

Address of Vervloet: Laboratoire de Photophysique Moléculaire du CNRS, Bâtiment 213, Université de Paris-Sud, 91405 Orsay, France.

TB1 (8:30)

SUB-DOPPLER INTRACAVITY LASER SPECTROSCOPY OF CoO AND VO

G. HUANG, D. J. CLOUTHIER AND A.J. MERER

A fluorescence cell inside the cavity of a standing wave dye laser has been used to record the hyperfine structure of some weak optical transitions of CoO and VO at sub-Doppler resolution. Second derivative line profiles with widths of 60 - 100 MHz could be obtained by detecting the Lamb dips with frequency modulation of the laser.

Portions of the three strongest sub-bands of CoO near 6400 Å have been recorded. These sub-bands are parallel-polarized, and have the $X^4\Delta$, $\Omega = 7/2$ and $5/2$ components as lower states; the upper states also have $\Omega = 7/2$ and $5/2$, but appear to belong to two different close-lying electronic states. Interpretation of the upper state hyperfine parameters is complicated by extensive mixing of the electronic states, but the negative value for the Fermi contact parameter in the ground state confirms that its electron configuration is $\sigma^2\pi^2\delta^3$.

A similar study of the hyperfine structure in the (1,0) band of the $B^4\Pi - X^4\Sigma^-$ system of VO near 7370 Å has been completed. The structure in the two least crowded and unperturbed sub-bands, $B^4\Pi_{5/2, 3/2} - X^4\Sigma^-$ has been analysed to show that the electron configuration of the $B^4\Pi$ excited state is $\pi\delta^2$.

Address of Huang and Merer: Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C. V6T 1Y6, Canada

Address of Clouthier: Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.

TB2 (8:47)

A NEW $^3\Pi$ ELECTRONIC STATE OF PtO.

C.L. Frum, R. Engleman, Jr., and P.F. Bernath¹

A new $^3\Pi$ electronic state of PtO has been observed between 7100 cm^{-1} and 8015 cm^{-1} above the $^3\Sigma^-$ ground state. The $^3\Pi_1 - ^3\Sigma_1^-$, $^3\Pi_1 - ^3\Sigma_1^-$, and $^3\Pi_2 - ^3\Sigma_1^-$ subbands were recorded in emission from a Pt Hollow cathode with the Fourier transform spectrometer associated with the McMath Solar Telescope at Kitt Peak. Molecular constants, including Ω -doubling parameters for the new electronic state, have been determined from the data.

Address of Frum, Engleman and Bernath: Department of Chemistry, University of Arizona, Tucson, AZ 85721

TB3 (8:59)

HIGH RESOLUTION FOURIER TRANSFORM INFRARED SPECTROSCOPY OF THE $A^3\Pi - X^2\Sigma$ TRANSITION OF CP.

R.S. Ram, S. Tam and P.F. Bernath

The near infrared emission spectrum of $A^3\Pi - X^2\Sigma$ transition of CP has been recorded using a Fourier transform spectrometer. The rotational structure of six new bands involving vibrational levels up to $v=4$ of both electronic states has been analyzed. The RKR potential energy curves for the $A^3\Pi$ and $X^2\Sigma$ electronic states have also been evaluated. This extends our previous work on CP¹.

¹ R.S. Ram and P.F. Bernath, *J. Mol. Spectrosc.* **122** 282(1987).

Address of Ram and Tam: Department of Chemistry, University of Arizona, Tucson, AZ 85721.

Address of Bernath: Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

TB4 (9:11)

LASER SPECTROSCOPY OF STRONTIUM MONOXIDE NEAR 8000 cm^{-1} :
ABSORPTION FROM THE LOW LYING $^1\Pi$ AND $^3\Pi$ STATES

R. F. W. HERRMANN and W. E. ERNST

The flame reaction $\text{Sr} + \text{N}_2\text{O}$ was investigated in a Broida-type oven by using laser excitation spectroscopy and dispersing the laser induced fluorescence with a $1/3\text{m}$ - monochromator.

Previously reported results about a transition near 16852 cm^{-1} involving a new triplet state at about 26300 cm^{-1} above the ground state could be improved.

A new bandhead at 16846 cm^{-1} was found and could be assigned to the transition $A' ^1\Pi - B ^1\Pi$. The observed wavelength of the bandhead is in good agreement with the value calculated from molecular data published by other groups [1]. Fluorescence from the $B ^1\Pi$ state into another excited state at about 9000 cm^{-1} above the ground state was observed (probably a $^3\Sigma$ state).

- [1] K. P. Huber and G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. IV, "Constants of Diatomic Molecules", Van Nostrand-Reinhold, New York 1979.

Address of Herrmann and Ernst: Department of Physics, Penn State University, 104 Davey Lab, University Park, PA 16802.

TB5 (9:23)

ANALYSIS OF THE $6100, 6900, \text{ AND } 10200\text{ CM}^{-1}$ RYDBERG-RYDBERG TRANSITIONS OF ArD

I. DABROWSKI, G. HERZBERG, J.W.C. JOHNS, D. SADOVSKII, and M. VERVOLET

The assignment of four emission bands of the ^{40}ArD molecule has been carried out successfully in terms of a common Rydberg state which is treated as a $p(^3\Pi, ^3\Sigma)$ -complex. In order to understand the structure of this complex and the corresponding selection rules it is vitally important to include the lxN -type Coriolis interaction along with the spin-orbit coupling. Two states, $^3\Pi$ and $^3\Sigma$, discovered several years ago by Johns [*J. Molec. Spectrosc.* **36**, 488 (1970)] are involved in the transitions.

Address: Herzberg Institute of Astrophysics, National Research Council, Ottawa, Canada K1A 0R6

TB6 (9:40)

HIGH RESOLUTION INFRARED FOURIER TRANSFORM EMISSION SPECTRUM OF THE N_2^+ MEINEL SYSTEM
 $A^2\Pi_u - X^2\Sigma_g^+$

D. W. FERGUSON, G. GUELACHVILI, P. A. MARTIN, AND K. NARAHARI RAO.

Although the $B^2\Sigma_u^+ - X^2\Sigma_g^+$ system of N_2^+ is well known, there have been only a few previous studies of the Meinel system ($A-X$).¹⁻⁴ Infrared emission spectra of the N_2^+ molecular ion have been recorded from $4000-11000\text{ cm}^{-1}$ at 0.013 cm^{-1} resolution using the Fourier transform interferometer of the Laboratoire d'Infrarouge, Orsay, France. The best signal-to-noise ratios were obtained using a hollow cathode source with flowing nitrogen although a positive column discharge was also used. Nine bands of the N_2^+ Meinel system were observed (0-0, 0-1, 0-2, 1-0, 1-1, 1-2, 1-3, 2-3), several for the first time and the others at higher resolution than recorded previously. Most of these bands have been subjected to a detailed spectral analysis to provide new, more precise molecular parameters for the $A^2\Pi_u$ and $X^2\Sigma_g^+$ states, especially the spin-rotation constant of the ground state which is difficult to determine from the B-X system. Equilibrium parameters are also determined in this analysis.

¹R. L. Gatteringer and A. Vallance Jones, *Can. J. Phys.* **51**, 287 (1973)

²W. Benesch, D. Rivers, and J. Moore, *J. Opt. Soc. Am.* **70**, 792 (1980)

³T. A. Miller, T. Suzuki, and E. Hirota, *J. Chem. Phys.* **80**, 4671 (1984)

⁴M. B. Radunsky and R. J. Saykally, *J. Chem. Phys.* **87**, 898 (1987)

Address of Ferguson and Rao: Department of Physics, The Ohio State University, Columbus, Ohio, 43210

Address of Martin and Guelachvili: Laboratoire d'Infrarouge, Université de Paris-Sud, Paris, France

Intermission

TB7 (10:10)

EUV ABSORPTION SPECTROSCOPY OF SUPERSONIC-JET-COOLED MOLECULES: N_2 BANDS IN THE WAVELENGTH REGION 95-100 nm

K. YOSHINO, K.P. HUBER, G. STARK, K. ITO, PETER L. SMITH, and W.H. PARKINSON

We have developed a supersonic jet expansion apparatus that is used with the 6.65-m vacuum spectrometer at the Photon Factory, KEK, Japan. A predispersed synchrotron radiation beam enters a 2-mm diameter hole close to the supersonic jet to define a section of the jet stream to record molecular absorption. Pure nitrogen or a mixture of nitrogen in helium is used. The absorption spectrum of N_2 at ~ 25 K in the wavelength region 95-100 nm has been investigated photographically and photoelectrically with this apparatus.

We have obtained the oscillator strengths of the $b^1\Pi_u - X^1\Sigma_g^+$ bands from absorption cross section measurements at very low temperature. These band oscillator strengths have been investigated by many authors, but only Lawrence *et al.*¹ pointed out that the measured cross sections can be severely affected by line saturation in these bands. Our results will be compared with previous work.

This work is supported by NASA grant NAGW 1596 to Harvard College Observatory.

¹G.M. Lawrence, D.L. Mickey and K. Dressler, J. Chem. Phys. **48**, 1989 (1968).

Address of Yoshino, Smith, and Parkinson: Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138

Address of Huber: Herzberg Institute of Astrophysics, NRC, Ottawa, Ontario K1A 0R6, Canada

Address of Stark: Physics Department, Wellesley College, Wellesley, MA 02181

Address of Ito: Photon Factory, KEK, Tsukuba, Ibaraki 305, Japan

TB8 (10:22)

FOURIER TRANSFORM SPECTROSCOPY IN THE VUV REGION, THE ABSORPTION BANDS OF NO

K. YOSHINO, A.P. THORNE, J.R. ESMOND, and W.H. PARKINSON

Fourier transform spectroscopy is a well established technique for measuring high resolution emission and absorption spectra with quantitative intensities. However, only the FTS at the Physics Department of Imperial College in London is suitable for operation in the VUV region. At the 44th Symposium on Molecular Spectroscopy we presented the results from this UVFTS of the Fourth Positive bands of CO in emission with the resolution of 0.08 cm^{-1} in the wavelength region 177-215 nm. We now present the results of measurements with the UVFTS of δ bands of NO in absorption. A high current hydrogen lamp is used as the background continuum source with a 0.3 m grating spectrometer as a bandpass filter. Absorption bands of $\delta(0,0)$ at 191 nm and $\delta(1,0)$ at 183 nm are studied at 295 K and 78 K with the resolution of 0.08 cm^{-1} . Rotational line assignments and band oscillator strengths of the both bands will be presented.

This work is supported by NSF grant ATM-87-17875 to Harvard College Observatory.

Address of Yoshino, Esmond, and Parkinson: Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138

Address of Thorne: Imperial College of Science and Technology, London SW7 2BZ, England

TB9 (10:34)

THE d-s STABILIZATION ENERGY OF THE RARE EARTH OXIDES AND FLUORIDES [Ba-Lu]
L.A. KALÉDIN, E.J. HILL, AND R.W. FIELD

Recent work has shown the success of the semiempirical and zero-free-parameter form of the ligand field model as applied to diatomic rare earth oxides and fluorides¹. We report here the results of the semiempirically calculated d-s energy shift of the center of gravity of the appropriate configurations of Ln^{2+} and Ln^{+2} which is relevant to the electronic structure of LnO and LnF .³

| Ln | free ion | | | molecule | | | d-s stabil. energy (cm^{-1}) |
|------------------|-----------|-----------|---------|-----------|-----------|---------|--|
| | $f^N d$ | $f^N s$ | differ. | $f^N d$ | $f^N s$ | differ. | |
| La | 961 | 13591 | -12630 | 11950 | 0 | 11950 | 24600 |
| Cd | 4939 | 10225 | -5276 | 11300 | 800 | 10500 | 15800 |
| Lu | 7472 | 0 | 7472 | 19800 | 0 | 19800 | 12300 |
| Ln ⁺ | | | | | | | |
| | $f^N d$ | $f^N s$ | differ. | $f^N d$ | $f^N s$ | differ. | |
| Ba | 5354 | 0 | 5354 | 11500 | 0 | 11500 | 6100 |
| Eu | 13393 | 730 | 12663 | 17000 | 620 | 16380 | 3700 |
| Ln ²⁺ | | | | | | | |
| | $f^N d s$ | $f^N s^2$ | differ. | $f^N d s$ | $f^N s^2$ | differ. | |
| La | 4593 | 7394 | -2801 | 4600 | 0 | 4600 | 7400 |
| Gd | 5474 | 3444 | 2030 | 6500 | 0 | 6500 | 4500 |

The d-s stabilization energy in LnO and LnF molecules decreases with increasing atomic number.

¹R.W. Field, Ber. Bunsenges. Phys. Chem. **86**, 771, (1982).

²C.E. Moore, Atomic Energy Levels as Derived from the Analysis of the Optical Spectra NSRDS-NBS 35, V.3 (1971); W.C. Martin, R. Zalubas, and L. Hagan, Atomic Energy Levels - the Rare Earth Elements, NSRDS-NBS-60 (1978).

³K.P. Huber and G. Herzberg, Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules, Van Nostrand Reinhold, (1979), N.Y.; L.V. Gurvich, Yu.N. Dmitriev, L.A. Kaledin, et al., Bull. Acad. Sci. USSR (Phys. Ser.), **53**, 75, (1989).

Address of Kaledin: High Temperature Institute of the USSR Academy of Sciences, Moscow, 127412. Visiting Scientist at Massachusetts Institute of Technology.

Address of Hill and Field: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139

TB10 (10:59)

THE LOW-LYING STATES OF THE URANIUM MONOXIDE (UO) MOLECULE
L.A. KALÉDIN

Recent work on the UO molecule in the gas phase¹ has led to the determination of the energies of five low-lying electronic states. Allowance for the stabilization of the outer 7s orbitals in relation to the inner 5f and 6d orbitals by the O^{2-} ligand field according to Field's method² shows that the lowest and first excited configurations of the bound ion in the $\text{U}^{2+} \text{O}^{2-}$ system are $5f^3 7s$ (configuration I) and $5f^2 7s^2$ (configuration II), respectively. In the fit procedure for the $5f^3 7s$ configuration, there were three variable parameters: the exchange interaction G_3 ($\approx 450 \text{ cm}^{-1}$) between the outer 7s and 5f core electrons and two crystal field parameters $B^2(6000 \text{ cm}^{-1})$ and $B^4(1500 \text{ cm}^{-1})$. B^6 was held fixed at 0 cm^{-1} . The spin-orbit interaction parameter ζ was set equal to the value for U^{+} in the $5f^3 7s^2$ configuration: $\zeta \approx 2100 \text{ cm}^{-1}$. The energies for the $5f^2 7s^2$ configuration (II) were calculated using the same values of the parameters as derived for the $5f^3 7s$ (I) configuration.

| con- fig. | energy | | con- fig. | energy | | con- fig. | energy | | con- fig. | energy | |
|--------------------|--------|-------|--------------------|--------|-------|--------------|--------|-------|--------------------|--------|-------|
| | exp. | calc. | | exp. | calc. | | exp. | calc. | | exp. | calc. |
| X 4 | I | 0 | (2) 3 | I | 1917 | (1) 6 | I | 4472 | (5) 3 | I | 5547 |
| (2) 4 | II | 294 | (3) 3 | II | 1928 | (2) 5 | I | 4585 | (4) 1 | I | 5567 |
| (1) 3 | I | 651 | (2) 2 | I | 2068 | (3) 5 | I | 4984 | (4) 0 [*] | I | 5585 |
| (1) 2 | I | 993 | (2) 1 | I | 2140 | (4) 4 | I | 5116 | (5) 2 | I | 5687 |
| (1) 5 | I | 1043 | (2) 0 ⁺ | I | 2160 | (5) 4 | I | 5314 | (5) 1 | I | 5754 |
| (1) 1 | I | 1117 | (3) 2 | II | 2818 | (4) 3 | I | 5378 | (5) 0 ⁺ | I | 5772 |
| (1) 0 ⁻ | I | 1146 | (3) 1 | II | 3233 | (4) 2 | I | 5505 | (6) 4 | II | 6918 |
| (3) 4 | I | 1574 | (3) 0 ⁻ | II | 3351 | (4) 5 | II | 5522 | (6) 3 | II | 7554 |

This table summarizes our results (in cm^{-1}) for the states of UO with energies less than 8000 cm^{-1} . [^{*} Energy of (2) 4 state fixed at observed value.]

¹L.A. Kaledin, A.N. Kulikov, A.I. Kobylanski, et al. Russ. J. Phys. Chem. **61**, 712, (1987).

²R.W. Field Ber. Bunsenges. Phys. Chem. **86**, 771 (1982).

Address: High Temperature Institute of the USSR Academy of Sciences, Moscow, 127412
Visiting Scientist at Massachusetts Institute of Technology sponsored by the US National Academy of Science and the Academy of Sciences of the USSR (NAS-ASUSR)

TB11 (11:16)

FOURIER TRANSFORM SPECTROSCOPY OF THE $1^3\Delta_g$ - $b^3\Pi_u$ TRANSITION IN $^6\text{Li}_2$. C. LINTON, R. BACIS, P. CROZET, F. MARTIN, A.J. ROSS, and J. VERGES

The $1^3\Delta_g$ - $b^3\Pi_u$ transition of $^6\text{Li}_2$, occurring in the visible region between 16000 - 20000 cm^{-1} , has been obtained at high resolution using Fourier Transform Spectrometers. The relaxed emission spectrum was observed via Collisionally Induced Fluorescence (CIF) following (a) excitation of the $\text{C}^1\Pi_u \leftarrow \text{X}^1\Sigma_g^+$ transition by UV lines of Argon and Krypton lasers, and collisional transfer from $\text{C}^1\Pi_u$ to $1^3\Delta_g$, or (b) excitation of $\text{F}^1\Sigma_g^+$ via $\text{F}^1\Sigma_g^+ \leftarrow \text{A}^1\Sigma_g^+ \leftarrow \text{X}^1\Sigma_g^+$ one colour double resonance using a CW ring dye laser, and transfer from $\text{F}^1\Sigma_g^+$ to $1^3\Delta_g$.

The spectra showed many lines which are broadened and shifted as a result of predissociation of $b^3\Pi_u$ by the $a^3\Sigma_g^+$ state and many examples of perturbations of $1^3\Delta_g$ by $2^3\Pi_u$. Line widths and shifts and rotational constants are shown to be compatible with ab-initio calculations. Details of these results, analysis of perturbations and examination of possible collisional propensity rules will be discussed.

Address of Linton: Physics Dept., University of New Brunswick, Fredericton, N.B., E3B 5A3, Canada.

Address of Bacis, Crozet, Martin and Ross: Laboratoire de Spectrometrie Ionique et Moléculaire, Université Claude Bernard, Lyon I, 43 boulevard du 11 Novembre 1918, 69622, Villeurbanne Cedex, France.

Address of Verges: Laboratoire Aimé Cotton, Centre National de la Recherche Scientifique II, Université de Paris-Sud (Paris XI), 91405, Orsay Cedex, France.

TB12 (11:33)

THE FIRST NEGATIVE (B-X) SYSTEM OF $^{13}\text{C}^{18}\text{O}^+$: PRECISE MOLECULAR CONSTANTS OF ITS $\text{X}^2\Sigma^+$, $\text{A}^2\Pi_1$ AND $\text{B}^2\Sigma^+$ STATES

C.V.V. PRASAD and S. PADDI REDDY

The $^{13}\text{C}^{18}\text{O}^+$ ions were excited in the cathode glow of a hollow-cathode discharge tube and the first negative ($\text{B}^2\Sigma^+ - \text{X}^2\Sigma^+$) system was recorded in the spectral region 2110-2755 Å. A total of 22 bands with $V'=0$ to 4 and $v''=0$ to 7 were observed under medium dispersion. The rotational structure of the 13 of these bands were recorded under high resolution on a 3.4 m Jarrell-Ash Ebert grating spectrograph using a 1200 grooves/mm grating in the fifth and sixth orders. The molecular constants derived from the analysis of the individual bands of this system were first merged together by the method of correlated least-squares fit. The resulting constants were then merged with those obtained from our recent studies on the comet-tail ($\text{A}^2\Pi_1 - \text{X}^2\Sigma^+$)¹ and the Baldet-Johnson ($\text{B}^2\Sigma^+ - \text{A}^2\Pi_1$)² systems of $^{13}\text{C}^{18}\text{O}^+$, and a precise set of molecular constants for the X, A, and B states was obtained. The vibrational constants for these three states and also the vibrational term values were obtained using the band origin data. The details of the analysis and the results obtained will be presented.

¹C.V.V. Prasad and S.P. Reddy, J.Chem.Phys. **90**, 3010 (1989).

²S.P. Reddy and C.V.V. Prasad, J.Chem.Phys. **91**, 1972 (1989).

Address of Prasad: Department of Chemistry, University of Waterloo, Waterloo, CANADA, N2L 3G1.

Address of Reddy: Department of Physics, Memorial University of Nfld, St. John's, CANADA, A1B 3X7

TB13 (11:50)**THE ELECTRIC DIPOLE MOMENT OF DYSPROSIUM MONOXIDE (DyO)**
C. LINTON and B. SIMARD

The Stark effect in the first lines, Q(8) and P(8), of the $\Omega = 7 \leftarrow \Omega = 8$ (ground state) transition of ^{164}DyO has been investigated at fields of up to 14 kV/cm. The transition was observed by laser induced fluorescence in a laser vaporization source. Spectra were obtained with the laser polarized both parallel and perpendicular to the field enabling us to obtain $\Delta M = 0$ and ± 1 transitions. Because of the high J, the spectra are complex (30 components with perpendicular polarization, 16 with parallel) and difficult to assign.

Details of the assignment and methods used to obtain the dipole moments for the two states will be presented and (perhaps) the results will be discussed in terms of the ligand field model for the electronic structure.

Address of Linton: Physics Department, University of New Brunswick, P.O. Box 4400, Fredericton, N.B., Canada, E3B 5A3.

Address of Simard: Laser Chemistry Group, Steacie Institute for Molecular Sciences, National Research Council, Ottawa, Ontario, Canada, K1A 0R6.

TC1 (8:30)

VIBRATIONAL SPECTROSCOPY OF *TRANS*-3,4-DIFLUOROCYCLOBUTENE

NORMAN C. CRAIG, SUSAN E. HAWLEY AND ANN PEARSON

The new substance, *trans*-3,4-difluorocyclobutene, has been obtained by distilling *cis*-3,4-dichlorocyclobutene through a short packing of a mixture of AgF₂ and KF. *cis*- and *trans*-3-chloro-4-fluorocyclobutene are isolatable intermediates. Very little of the *cis* isomer of difluorocyclobutene is formed in this reaction.

From gas-phase and glassy-phase infrared spectra and a liquid-phase Raman spectrum, a complete assignment of the vibrational fundamentals of *trans*-3,4-difluorocyclobutene has been made. This molecule has C₂ symmetry and has an estimated κ of -0.47. The totally symmetric modes have B-type shapes in the gas-phase infrared spectrum. The fundamentals are in cm⁻¹: (a) 3106, 2977, 1559, 1354, 1193, 1169, 1143, 1038, 993, 931, 601, 309, 184; (b) 3088, 2977, 1332, 1298, 1198, 1064, 970, 844, 684, 426, 326. Correlations with the assignments for *trans*-3,4-dichlorocyclobutene are good.¹ The ring-puckering mode of 184 cm⁻¹ fits well the emerging pattern for halogen-substituted cyclobutenes.

¹N. C. Craig, S. E. Hawley and C. L. Perry, *Spectrochim. Acta*, 47, 000 (1991).

Address of authors: Department of Chemistry, Oberlin College, Oberlin, OH 44074.

TC2 (8:41)

FAR-INFRARED SPECTRA AND TWO-DIMENSIONAL POTENTIAL ENERGY SURFACE FOR THE RING-TWISTING AND RING-BENDING VIBRATIONS OF CYCLOHEXENE AND ITS DEUTERATED DERIVATIVES.

S. J. LEIBOWITZ, V. E. RIVERA-GAINES, AND J. LAANE

The far-infrared and Raman spectra of cyclohexene and five of its deuterated derivatives have been recorded. In the gas-phase infrared spectrum of cyclohexene, two series of bands originating at 165 cm⁻¹ and 276 cm⁻¹ were assigned to the ring-bending and ring-twisting vibrations, respectively. Overtone, sum, and difference bands provided additional data for the assignment of the energy states. A potential energy surface of the form

$$V = a_1x_1^4 + b_1x_1^2 + a_2x_2^4 + b_2x_2^2 + cx_1^2x_2^2$$

was used to represent the potential energy surface, and appropriate kinetic energy expansions were determined for these computations. Cyclohexene has a twisted (half-chair) conformational minimum. The planar and bent conformations were calculated to be 4700 and 1100 cm⁻¹ higher in energy, respectively. These results will be compared to those recently determined for related oxygen containing compounds.¹

¹ M. M. Tecklenburg and J. Laane, *J. Am. Chem. Soc.*, 111, 6920 (1989).

Address of Leibowitz and Laane: Texas A&M University, College Station, TX 77843.

Address of Rivera-Gaines: Bristol-Meyers, USBNG, Evansville, IN 47721.

TC3 (8:57)

FAR-INFRARED SPECTRA AND TWO-DIMENSIONAL RING-BENDING POTENTIAL ENERGY SURFACE OF 1,3-OXATHIOLANE

S. J. LEIBOWITZ, J. R. VILLARREAL, AND J. LAANE

The far-infrared spectra of the five-membered ring 1,3-oxathiolane have been recorded and analyzed. A series of well-defined bands due to the ring-bending (hindered pseudorotation) vibration originate at 110 cm^{-1} . These are separated by about 10 cm^{-1} and extend down to 33 cm^{-1} . A second series of bands near 314 cm^{-1} arise from the ring-twisting (radial) mode. Sum, difference, and combination bands between the twisting and bending vibrations have also been observed and these provide a definitive assignment for all of the low-lying energy states. The pseudorotational series can be fit using a one-dimensional periodic potential and a barrier to pseudorotation of 500 cm^{-1} . However, the two-dimensional potential surface derived for this molecule provides a more complete picture of the conformational energetics. The calculations were aided by the determination of the appropriate kinetic energy expansions for the two out-of-plane ring motions.

Address of Leibowitz and Laane: Texas A&M University, College Station, TX 77843.

Address of Villarreal: Pan American University, Edinburg, TX 78539.

TC4 (9:08)

REINVESTIGATION OF THE FAR-INFRARED SPECTRA OF THE OUT-OF-PLANE VIBRATIONS OF 1,3-DIOXOLANE

E. CORTEZ AND J. LAANE

The out-of-plane ring vibrations of 1,3-dioxolane have previously been investigated. These modes can be represented by a nearly free pseudorotation and a radial motion. We have initiated a reinvestigation of the far-infrared spectra of this molecule in order to determine a two-dimensional potential energy surface for the out-of-plane modes. Pseudorotational bands have been observed in the $30\text{-}120\text{ cm}^{-1}$ range and the radial vibration in combination with various pseudorotational states gives rise to spectra between 140 and 360 cm^{-1} . The perturbation effect of a small barrier to pseudorotation on the lower pseudorotational energy levels has been examined. These results will be compared to those of 1,3-oxathiolane.

Address: Department of Chemistry, Texas A&M University, College Station, TX 77843

TC5 (9:19)

ANALYSIS OF THE TRANSITION FROM NORMAL MODES TO LOCAL MODES

S. ABBATE, G. LONGHI, C. ZAGANO, G. BOTTO, D. GHISLETTI, L. LESPADÉ

By numerical integration of the classical equations of motion for a system of two coupled anharmonic oscillators, one can define the vibrational motions as follows: normal modes, for which energy is exchanged between the two oscillators and their phase difference is almost constant; local modes, for which the energy of one oscillator is always greater than the other's and their phases are independent (1).

We found a third type of modes, that we called transition modes, which show phase relation between the two oscillators and yet no energy exchange. They appear at total energy values intermediate between those typical for normal modes and for local modes. We tested our finding by two perturbative approaches, based on local modes and normal modes respectively.

In this note we will point out the parameters favoring a wide extent of transition modes, in order to look for a spectroscopic signature of such modes.

¹E.L.Sibert III, W.P.Reinhardt, J.T.Hynes, J. Chem. Phys., 77,3583(1982)

Address of Abbate and Longhi: Dipartimento di Chimica Fisica, Università di Palermo, via Archirafi 26, 90123 Palermo, Italy.

Address of Ghisletti, Zagano, Botto: Dipartimento di Fisica, Università di Milano, via Celoria 16, 20133 Milano, Italy.

Address of Lespadé: Laboratoire de Spectroscopie Moléculaire et Cristalline, Université de Bordeaux I, 351 Crs. de la Libération, 33405 Talence, France.

TC6 (9:35)

CONFORMATIONAL STABILITY, BARRIERS TO INTERNAL ROTATION, VIBRATIONAL ASSIGNMENT, AND AB INITIO CALCULATIONS OF TRANS-1,3-DICHLOROPROPENE

T. G. Costner, T. S. Little, J. R. Durig, and D. T. Durig

The far infrared spectrum of gaseous *trans*-1,3-dichloropropene has been recorded at a resolution of 0.10 cm⁻¹ in the region of 350 - 50 cm⁻¹. The fundamental asymmetric torsional frequencies of the more stable *gauche* and the higher energy *cis* conformations have been observed at 85 and 130 cm⁻¹, respectively. Several excited states falling to lower frequencies were observed for the *cis* conformation. From these data the asymmetric torsional potential function governing the internal rotation about the C-C bond has been determined. From studies of the Raman spectrum at variable temperatures, the conformational enthalpy difference has been determined. A complete assignment of the vibrational fundamentals observed from the infrared spectra (3300 - 50 cm⁻¹) of the gas and solid and the Raman spectra (3200 - 10 cm⁻¹) of all three physical states is proposed. All of these data are compared to the corresponding quantities obtained from *ab initio* Hartree-Fock gradient calculations employing both the 3-21G* and 6-31G* basis sets.

Address of Costner, Little, and J. R. Durig: Department of Chemistry, University of South Carolina, Columbia, SC 29208, USA

Address of D. T. Durig: Departments of Chemistry and Physics, The University of the South, Sewanee, TN 37375, USA

Intermission

TC7 (10:05)

Perturbative treatments of Highly Excited Rotation-Vibration States using Curvilinear Coordinates

Darin C. Burleigh, Anne B. McCoy and Edwin L. Sibert III

Abstract

The methods previously developed in this group to study vibrational states in polyatomic molecules using Canonical Van Vleck Perturbation Theory (CVPT)¹ are extended to include rotational interactions and applied to H₂O, SO₂ and H₂CO. For these calculations, we use a Taylor series expansion of the general Hamiltonian derived by Pickett.² In applying CVPT, it is computationally convenient to take advantage of the isomorphism between the SU(2) and SO(3) groups, rewriting the angular momentum operators in terms of harmonic oscillator raising and lowering operators. Calculated energies for H₂O and SO₂ agree well with variationally obtained energies up to 19,000 cm⁻¹ and 11,000 cm⁻¹, respectively. Since we use an analytical expression of the Hamiltonian for these variational calculations, comparison between the variational and perturbative energies provides a check on both the techniques used to obtain the expansions and the convergence of the perturbative results. Further, for H₂CO, we find that careful description of the internal curvilinear bend coordinates extends the energy regimes over which these calculations are tractable. Proper choice of these coordinates leads to improved convergence in the perturbative energies, sixth order rotation-vibration energies are converged to 8,000 cm⁻¹, and makes high quality variational calculations tractable for vibrational states with energies up to 10,000 cm⁻¹ above the zero point.

¹E. L. Sibert, J. Chem. Phys. **88**, 4378 (1988)²H. M. Pickett, J. Chem. Phys. **56**, 1715 (1972)

Address: Department of Chemistry and Theoretical Chemistry Institute, University of Wisconsin - Madison, Madison, WI 53706

TC8 (10:21)

Investigating the Separability of Vibrational Motions

Rudolph C. Mayrhofer and Edwin L. Sibert III

Abstract

Colbert and Sibert have investigated a class of coordinates, called the Variable Curvature Coordinates (VCC), in which the curvature of the coordinates for various model problems was varied to find the most separable representation possible.¹ This work is now extended to SO₂ and H₂O. Using Distributed Gaussian Basis sets, vibrational SCF and adiabatic eigenvalues are calculated as a function of the VCC in order to examine the separability of the vibrational wavefunctions. The natural models of the variational wavefunction are also constructed and provide an alternative means of describing the separability of the coordinates.

¹D. T. Colbert and E. L. Sibert III, J. Chem. Phys. **91**, 350 (1989)

Address: Department of Chemistry and Theoretical Chemistry Institute, University of Wisconsin - Madison, Madison, WI 53706

TC9 (10:37)

Calculation of IR Intensities of Highly Excited Vibrational States in HCN Using Van Vleck Perturbation Theory

Anne B. McCoy and Edwin L. Sibert III

Abstract

Canonical Van Vleck perturbation theory (CVPT) is used to calculate electric dipole intensities for one, two, and three-dimensional models of HCN. Lehmann and Smith¹ have illustrated that the intensities of overtone transitions are sensitive to the details of the inner wall of the potential. Dipole intensities calculated for several, similar one-dimensional CH stretch potentials demonstrate that perturbation theory correctly predicts this sensitivity. The perturbative intensities of a two-dimensional *ab initio* dipole surface indicate the importance of selected stretch-stretch resonance interactions in interpreting the CH stretch overtone spectra of HCN. The inclusion of the bend confirms that this degree of freedom plays a significant role in weakening the intensity of the CN overtones. In all these calculations the perturbative results are in excellent agreement with the corresponding variational results.

¹K. K. Lehman and A. M. Smith, J. Chem. Phys. **93**, 6140 (1990)

Address: Department of Chemistry and Theoretical Chemistry Institute, University of Wisconsin - Madison, Madison, WI 53706

TC10 (10:53)

REDUCED MASS OF RING PUCKERING AS A FUNCTION OF PUCKERING COORDINATES FOR RING MOLECULES

Wenyun Zhao and J. R. Durig

The reduced mass of the ring puckering motions for some four-membered ring molecules has been calculated based on the structural parameters obtained from *ab initio* geometry optimization calculations corresponding to a series of individual puckering angles. The dependence of the reduced mass on the puckering coordinate is considerably different from previous studies where the ring deformation and rocking parameter were assumed to be constant. By using the reduced mass function in the expression for the kinetic energy and Gaussian-polynomial potential function, the solutions of the ring puckering Hamiltonian reproduce the frequencies of hot bands of puckering transitions very well. Moreover, the puckering angle determined from this potential function agrees with the angle obtained from other structural studies.

Address: Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208, USA

TC11 (11:04)

SF₆ GAS INTEGRATED INTENSITIES AS A FUNCTION OF DENSITY

GORINNE T. DELAYE AND MICHAEL E. THOMAS

Index of refraction measurements on SF₆ at microwave and visible frequencies suggest that collision-induced-absorption bands (CIA) should be present in SF₆, in addition to the ir-allowed bands. This would explain the density dependence of the index measurements /1/. Integrating the absorption coefficient $k(\nu)$ over the entire vibrational band yields the integrated intensity, which is related to the absorber density ρ by:

$$\int k(\nu) d\nu = \alpha_1 \rho + \alpha_2 \rho^2$$

where α_1 is the linear integrated absorption coefficient and represents the allowed band contribution and α_2 is the binary integrated absorption coefficient and represents the CIA band contribution. Previous measurements have been made at high densities /2,3/. However, low density measurements are also needed to substantiate the existence of CIA bands. A 10 meter White cell is used to collect data with a Fourier Transform Spectrometer. Assuming a linear law ($\alpha_2=0$), in the $3\nu_3$ band, the coefficient α_1 is larger at high densities than at low densities. The relative difference is about 10%. A quadratic law is used to fit the data for this band ($\alpha_1=2641.5$ cm/mol and $\alpha_2=3.38e5$ cm²/mol²). Accuracy of the integrated intensities is less than 2%, and the relative errors between our experimental data and data obtained with the quadratic law are less than 4.5%. Therefore, for the $3\nu_3$ band, contributions of CIA to the band intensity appear to be larger than the experimental uncertainty.

/1/ G. Birnbaum and T.K Bose, J. Chem Phys 71, 17 (1979).

/2/ C. Chapados and G. Birnbaum, J. Molec. Spectrosc. 132, 323 (1988).

/3/ M.E Thomas and M.J. Linevsky, J. Quant. Spectrosc. Transfer. 42, 465 (1989).

Address: Applied Physics Laboratory, The Johns Hopkins University,
Laurel Md 20723

TC12 (11:20)

CONTINUUM ABSORPTION MEASUREMENTS AND LINE SHAPE MODEL COMPARISONS

MICHAEL E. THOMAS AND CORINNE T. DELAYE

Absorption spectra of H₂O are recorded in different spectral window regions with a Fourier Transform Spectrometer and a high temperature-high pressure cell. Pure CO₂ and N₂ broadened CO₂ spectra are also obtained in the 4.1 μ m region where far wing absorption dominates. In this case a 10 meter White cell is also used which allows lower density measurements to be made.

Birnbaum's line shape /1/ is used to represent the far wing absorption of CO₂ and H₂O. The theory is semiempirical and does not include line mixing. Corrections which account for line mixing contributions are needed to obtain agreement with experiment. Justification for these corrections will be given.

/1/ G. Birnbaum, J. Quant. Spectrosc. Radiat. Transfer 21, 597 (1979).

Address: Applied Physics Laboratory, The Johns Hopkins University,
Laurel, MD 20723

TC13 (11:36)

PIEZOELECTRIC DETECTION OF OVERTONE SPECTRA OF LIQUIDS WITH C.W. LASER EXCITATION. CARLOS MANZANARES and VICTOR BLUNT.

To study overtone absorptions in condensed phases, a technique is presented which uses a piezoelectric detector, lock-in amplification and a C.W. dye laser modulated at frequencies from 10 kHz to 120 kHz with an acousto-optic modulator. Acoustic resonance frequencies calculated for a cylindrical cell are observed experimentally using liquid Si(CH₃)₄ as the sample. The acoustic signal is found to be proportional to the laser power. The $\Delta v = 5, 6$, and 7 overtones of the C-H stretching mode of Si(CH₃)₄ have been recorded. The sensitivity of the technique is discussed.

Carlos Manzanares and Victor Blunt: Department of Chemistry, Baylor University, Waco, TX 46498.

TC14 (11:52)

CANCELLED

INFRARED AND RAMAN SPECTRA AND VIBRATIONAL ANALYSES OF CYCLOPENTADIENYL THALLIUM V. A. MEIER AND D. P. McDERMOTT

Complete vibrational analyses of Cyclopentadienyl (CPDA) thallium have been performed resulting in two different simple valence force fields.

One force field was obtained from a fit to MOPAC/MINDO generated vibrational frequencies. The other force field is a set of true empirical force constants obtained from fitting to IR and Raman-observed frequencies. Comparison of the two force fields shows them to be remarkably similar.

The Raman spectrum of CPDA thallium is interesting and singular because it has unusually narrow and sharp C-C stretching bands which have only been observed before in IR spectra of CPDA-metal compounds.

Although CPDA-thallium is believed to be a simple ionic salt in the solid phase¹, explanation of the Raman spectrum can be provided only through the assumption of a "sandwich" compound to some extent in the solid phase.

¹E. Frasson, E. Menegus and C. Panattoni, Nature, 199, 1087 (1963).

Address of Meier: New Jersey Medical College, Newark, NJ.

Address of McDermott: Division of Science and Math, Lees College, Jackson, Kentucky 41339.

TE1 (1:30)

The Rotationally Resolved, Near Infrared Spectrum of the Argon-Methylacetylene van der Waals Complex

Thomas A. Blake, Shao-Hui Tseng, Marius Lewerenz, Paul Swift, and Robert O. Watts.

A molecular beam/optothermal detection technique and F-center laser system have been used to obtain the rotationally resolved, near infrared spectrum of the argon-methylacetylene van der Waals complex in the vicinity of the $\nu = 1$, C - H stretch of the methylacetylene monomer at 3335 cm^{-1} . Of the ca. 140 transitions observed (linewidths 15 - 20 MHz fwhm), 59 have been assigned to an A internal rotor state, b-type spectrum of the complex. These transitions have been fit using a Watson A reduction Hamiltonian in a P representation. The fit constants for the A state are: $A' = 0.2910(2) \text{ cm}^{-1}$, $B' = 0.06109(7)$, $C' = 0.05000(4)$, $A'' = 0.2939(4)$, $B'' = 0.06127(8)$, $C'' = 0.04991(6)$, $\nu_0 = 3334.5220(5) \text{ cm}^{-1}$. The A state band center is red shifted from the monomer band center by $0.5374(8) \text{ cm}^{-1}$. A preliminary estimate of the complex's structure (estimate based on $(B + C) / 2$ and B - C values of trial structures) has the angle between the symmetry axis of the methylacetylene and a line connecting the triple bond center to the argon at 90° and the length of this line as 3.60 Å.

Address of Authors: Department of Chemistry BG-10, University of Washington, Seattle, Washington 98195.

TE2 (1:47)

CORIOLIS COUPLING IN THE LOWEST π STATE OF Ar-HBr AND Ar-HCl

S.W. Reeve, M.A. Dvorak, D.W. Firth, and K.R. Leopold

The P and R branches of the lowest π bending vibration of Ar-HBr and Ar-HCl have been observed using a tunable far infrared spectrometer coupled to a planar free jet expansion. In conjunction with existing microwave data, and with previous measurements on the Q branches of these transitions, the measurements provide the J-dependence of the ℓ -type doubling splittings in the π state. For Ar-HBr, the splittings are a highly nonlinear function of $J(J+1)$, indicating the presence of another state which is Coriolis coupled to, and fortuitously near-degenerate with the π state. The implications of this result are discussed in relation to the best available potential energy surface for the system. For Ar-HCl, the rovibrational frequencies for the π bend are analyzed simultaneously with existing data for the Σ bend and Σ stretch to give deperturbed rotational constants and Coriolis coupling parameters. The deperturbed rotational constants for the Σ bend of the ^{35}Cl and ^{37}Cl species are discussed in terms of the predicted antihydrogen bonded geometry for that state, and the Coriolis coupling constants are compared with those previously measured on the $\text{HCl}(v=1)$ potential surface.

Address of Reeve, Dvorak, and Leopold: Department of Chemistry, University of Minnesota, Minneapolis, MN 55455

Address of Firth: Tennessee Eastman Corporation, Kingsport, TN 37662

TE3 (2:04)

POTENTIAL ANISOTROPY AND THE INFRARED SPECTRA OF H_2 -CO AND H_2 - N_2 VAN DER WAALS COMPLEXES

Claudio Chuquiqui and Robert J. Le Roy

Fully-resolved infrared spectra of the weakly bound diatom-diatom Van der Waals complexes H_2 -CO and H_2 - N_2 have recently been measured by McKellar.¹ An essential first step towards the determination of accurate potential energy surfaces for such systems is obtaining an understanding how their energy level patterns depend on the anisotropy of the associated potential energy surfaces.

Because of the large rotational level spacing and near-spherical nature of diatomic hydrogen, to a (good!) first approximation the energy level patterns of $H_2(j=0)$ -(diatom) complexes are qualitatively very similar to those formed between that diatom and a structureless atom. As a result, we may use analogies with (atom)-(diatom) complexes for which realistic potential energy surfaces are available, and generate plausible trial spectra for the $H_2(j=0)$ -(diatom) species of interest. In this paper, we use this approach to investigate the effect of the CO and N_2 anisotropy on predicted infrared spectra for the $H_2(j=0)$ -CO and $H_2(j=0)$ - N_2 Van der Waals complexes. The results of this study and the validity of this simplified approach will be discussed, with emphasis being placed on the question of how to utilize such results to facilitate the determination of *full* potential energy surfaces for such systems.

¹ A.R.W. McKellar, *J. Chem. Phys.* 93, 18 (1990).

Address: Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

TE4 (2:21)

AN "ITERATIVE SECULAR EQUATION" METHOD FOR CALCULATING ROVIBRATIONAL STATES OF WEAKLY-BOUND COMPLEXES

Tom Slee and Robert J. Le Roy

A new method for calculating rovibrational states of weakly-bound complexes from a given multi-dimensional potential surface is described and tested. This "iterative secular equation" (ISE) method generates eigenvalues and wave functions for a few states at a time, which makes it particularly useful for simulating Van der Waals spectra, and for use in least-squares fitting to such spectra to determine potential energy surfaces. The ISE method is in principle exact for bound states, and it yields reliable estimates of the energies and widths of metastable levels. The range of applicability of the ISE method is demonstrated by application to complexes such as $He-C_2H_2$, $He-HF$, $Ar-HCN$, and $Ar-HCl$. The ISE method is also shown to be more efficient than certain other coupled-channel or basis-set methods, for many problems.

Address: Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

TE5 (2:38)

DEVELOPMENT OF A FULL 3-DIMENSIONAL POTENTIAL ENERGY SURFACE FOR He - HF FROM HIGH-RESOLUTION SPECTROSCOPY

Tom Slee and Robert J. Le Roy

All previous potential energy surfaces determined for (alkali halide)-(rare gas) dimers have treated the diatom as a rigid rotor. However, the recent high-resolution near-infrared spectra of He - HF and He - DF reported by Lovejoy and Nesbitt provide data from which we are developing a *full* potential energy surface, including the HF stretching degree of freedom, by performing direct least-squares fits to the experimental data. This analysis exploits the ability of our recently-developed ISE method to rapidly and accurately generate energies and widths for bound and metastable states. Our determination of an anisotropic and stretching-dependent potential energy surface using the ISE method will be described.

Address: Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

TE6 (2:55)

SPECTROSCOPIC DIAGNOSTICS FOR TEMPERATURE, CLUSTER SIZE AND DEGREE OF SOLVATION IN INHOMOGENEOUS VAN DER WAALS CLUSTERS

Mary Ann Kmetz and Robert J. Le Roy

Recent experiments by Scoles et al.¹ on the spectroscopy of rare gas clusters containing an infrared active chromophore such as SF₆ or Si₄, suggest that for different solvent/solute combinations, the impurity may find itself preferentially either buried *inside* the cluster, or sitting *on its surface*. Previous theoretical work suggests that a characteristic doublet they observe in the infrared spectra of moderately large ($n \geq 10^3$) SF₆-(Ar)_n clusters is due to the SF₆ being only partially immersed in the bath of perturbing Ar atoms. The present paper reports the results of recent simulations designed to associate features of such spectra with the degree to which the solute chromophore molecule is immersed in the rare gas solvent, and the temperature and size of these clusters.

¹ G. Scoles, private communication (1991).

Address: Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

Intermission

TE7 (3:27)

TUNNELING SPLITTINGS IN A-BX₄ TYPE VAN DER WAALS MOLECULES
NOBUKIMI OHASHI AND JON T. HOUGEN

Takami and Jörissen¹ have observed an infrared diode-laser spectrum of Ar-SiF₄ showing complicated features which may arise from internal motions. Analysis of the spectrum is hindered at present, however, by strong overlapping lines from the SiF₄ monomer. Kawashima and Hirota² have studied the microwave spectrum of Na-BH₄ in the gas phase. Although this spectrum does not appear to show tunneling splittings in the ground vibrational state, such splittings may well appear in vibrationally excited states.

Motivated by these observations we have undertaken a theoretical study to parameterize tunneling-rotational energy level expressions and predict tunneling splitting patterns in weakly bound A-BX₄ type complexes, provided that the internal motions correspond to tunneling through relatively high barriers separating the various equilibrium frameworks. Because the spherical top subunit can internally rotate about axes pointing in a number of different directions, this type of complex is well suited for application of the formalism originally developed for the water dimer.

The number of frameworks between which tunneling occurs will depend on the equilibrium geometry of the complex, possible numbers of frameworks being 4, 6, 12, or 24. The lowest number of frameworks arises when the complex has the highest (C_{3v}) symmetry, i.e., when atom A is located at the center of a face of the BX₄ tetrahedron, or directly above one vertex. The highest number of frameworks arises when the complex has no symmetry, i.e., when the atom A is located off-center on a face or not directly above a vertex. In the present study we consider only the C_{3v} case, with its four equilibrium frameworks. We further assume that the tetrahedral structure of the BX₄ subunit remains unaltered during the large-amplitude internal-rotation tunneling motion.

In the talk we describe a coordinate system for the large-amplitude motion, together with the associated G₂₄ group theoretical formalism, basis set functions, and Hamiltonian matrix. We also present some possible two-parameter splitting patterns.

¹M. Takami and L. Jörissen, private communication.

²Y. Kawashima and E. Hirota, 1990 Molecular Structure Symposium, Kyushu University, Japan.

Address of Ohashi: Department of Physics, Faculty of Science, Kanazawa University, Kanazawa 920, Japan

Address of Hougén: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

TE8 (3:44)

MICROWAVE SPECTRUM AND STRUCTURE OF THE KETENE—ETHYLENE COMPLEX: AN EXAMPLE OF THE $2\pi + 2\pi$ CYCLOADDITION REACTION

F. J. LOVAS, R. D. SUENRAM, C.W. GILLIES, AND J. Z. GILLIES

The microwave spectrum of the $\text{CH}_2\text{CO—CH}_2=\text{CH}_2$ complex was observed in a pulsed-beam Fourier transform microwave spectrometer. In addition to the normal isotopic species, which exhibits a b-type rotational spectrum and four states due to internal motions, complexes of ketene with *trans*- CHD=CDH and $\text{CD}_2=\text{CH}_2$ have been observed and these also exhibit four states, while the ketene—*cis*- CHD=CHD species exhibits two states. Spectral analysis yields the rotational constants for $\text{CH}_2\text{CO—CH}_2=\text{CH}_2$:

$A = 7494.141(2)$ MHz, $B = 2276.441(6)$ MHz, and $C = 1966.992(6)$ MHz.

The structural analysis, assuming fixed monomer geometries, shows that the ketene unit lies in the *a,b*-plane of the complex and the symmetry axis of ethylene is parallel to the *c*-axis, i.e. the symmetry axis of the two units are crossed at 90° , with a center of mass separation, R_{cm} , of 3.46 Å. Stark effect measurements for the normal isotopic species provide the dipole moment components $\mu_a = 0$ D, $\mu_b = 1.376(1)$ D and $\mu_c = 0$ D which are consistent with the structural results. Further details concerning the tunneling motions and structure analysis will be given. Comparisons with related complexes, such as ketene-acetylene, and cycloaddition prototype species will be presented.

Address of Lovas and Suenram : Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

Address of C. W. Gillies : Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180

Address of J. Z. Gillies : Department of Chemistry, Siena College, Loudonville, NY 12221

TE9 (4:01)

MICROWAVE SPECTRUM AND STRUCTURE OF THE OC—SO_2 COMPLEX

F. J. LOVAS AND R. D. SUENRAM

The microwave spectrum of the OC—SO_2 complex was observed in a pulsed-beam Fourier transform microwave spectrometer and exhibits an *a*- and *c*-type rotational spectrum. In addition to the normal isotopic species, the $^{34}\text{SO}_2$ and ^{13}CO substituted isotopic species were studied in natural abundance. Spectral analysis yields the rotational constants for OC—SO_2 :

$A = 8869.377(3)$ MHz, $B = 1495.699(1)$ MHz, and $C = 1332.206(1)$ MHz. Further work is in progress on the spectrum of the C^{18}O isotopic form.

Stark effect measurements for the normal isotopic species provide the dipole moment components $\mu_a = 0.321(1)$ D, $\mu_b = 0$ D and $\mu_c = 1.600(2)$ D. The structural analysis, assuming fixed monomer geometries, shows that the CO unit and the symmetry axis of SO_2 lie in the *a,c*-plane of the T-shaped complex and the oxygen atoms of SO_2 are located symmetrically perpendicular to the *a,c*-plane. The center of mass separation, R_{cm} , is 4.059(1) Å and the C-S distance is 3.506 Å with the carbon atom participating in the van der Waals bond. Further details concerning the spectral and structure analysis will be given. Comparisons with related complexes will be presented.

Address of Lovas and Suenram : Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

TE10 (4:13)

ROTATIONAL SPECTRUM OF THE METHANE-WATER VAN DER WAALS COMPLEX.

R. D. SUENRAM, G. T. FRASER, AND F. J. LOVAS

Using rotational constants obtained by Busarow and co-workers in their ground breaking work on the far infrared spectrum of the $\text{CH}_4\text{-H}_2\text{O}^1$ we have located nine $J=2-1$ rotational transitions in the region of 17-17.6 GHz using a pulsed-nozzle Fourier-transform microwave spectrometer. A careful analysis of first and second order Stark effects displayed by these transitions allows us to confirm a number of the symmetry state labels previously assigned by Busarow and co-workers¹ for some of the rotational-internal rotor states observed. Electric dipole moments determined from the various transitions range from $\mu_a = 0.6$ to 0.8 Debye. A discussion of these Stark effect measurements will be presented.

¹ K. L. Busarow, R. C. Cohen, C. A. Schuttenmaer, Y. T. Lee, and R. J. Saykally, 45'th Sym. on Mol. Spectrosc., 1990, TA10 and private communications.

Address of Suenram, Fraser, and Lovas : Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

TE11 (4:30)

DEUTERATED-ACETYLENE DIMERS: THE TUNNELING MOTIONS OF $(\text{DCCD})_2$, $(\text{DCCH})_2$, DCCD-DCCH , DCCH-DCCD , HCCH-DCCD , AND HCCH-DCCH FROM THEIR MICROWAVE SPECTRA

K. MATSUMURA, F. J. LOVAS, R. D. SUENRAM

The rotational spectra of deuterated acetylene dimers, which were produced in a molecular beam at 1 K using 1:1 mixtures of HCCH, DCCD, and DCCD in Ar, were observed with a pulsed-beam Fourier transform microwave spectrometer. All types of the deuterated acetylene dimers in which a D atom participates in the hydrogen-bond were observed, i.e. $(\text{DCCD})_2$, $(\text{DCCH})_2$, DCCD-DCCH , DCCH-DCCD , HCCH-DCCD , and HCCH-DCCH . However, we could not detect any form of the mixed H/D dimers in which the hydrogen atom is located in the hydrogen-bond. From the interconversion tunneling spectra, the tunneling potential of $(\text{DCCD})_2$ was analyzed by using a one-coordinate model (Fraser *et al.*¹) and the potential depth was determined to be $V_4 = 35.577 \text{ cm}^{-1}$, which is 2.371 cm^{-1} deeper than that of $(\text{HCCH})_2$ studied by Fraser *et al.*¹. Also we applied a modified version of the one-coordinate model was also applied to the other deuterated acetylene dimers. A discussion of the observed spectra and tunneling model will be presented.

¹ G. T. Fraser, R. D. Suenram, F. J. Lovas, A. S. Pine, J. T. Hougen, W. J. Lafferty, and J. S. Muentz, J. Chem. Phys. 89, 6028 (1988).

Address of Lovas and Suenram : Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

Address of Matsumura : Seinan Gakuin University, Nishijin, Sawaraku, Fukuoka 814, Japan

TE12 (4:47)

DISSOCIATION OF B STATE I_2 INDUCED IN VAN DER WAALS COMPLEXES

M. L. Burke and W. Klemperer

Electronic predissociation of the B state of van der Waals complexes of I_2 has been studied via simultaneous optical absorption and laser induced fluorescence measurements in a planar jet. The complexing partner of I_2 induces mixing of the bound B state with nearby repulsive states to induce I-I bond cleavage and thus fluorescence quenching. Absolute values of fluorescence quantum yields are obtained by normalizing fluorescence and absorption spectra for the complexes to those of uncomplexed I_2 . The magnitude of the electronic state coupling has been probed as a function of the strength of the van der Waals bond by varying the complexing partner of I_2 .

Address of Burke and Klemperer: Dept. of Chemistry, Harvard University, Cambridge, MA 02138

TE13 (5:04)**STRUCTURE AND INTERNAL MOTION OF COMPLEXES OF NCCN WITH NCCN, NH₃, AND H₂O**

I. Suni, S. Lee, and W. Klemperer

Microwave and radiofrequency spectra have been obtained for the complexes of NCCN with itself, with NH₃ and with H₂O. All three systems are T-shaped with the heavy atoms in a C_{2v} arrangement and all yield spectra perturbed by internal motion. The NH₃ subunit in NH₃-NCCN exhibits nearly free internal rotation with respect to the NCCN framework, whereas the H₂O subunit in H₂O-NCCN has a moderate torsional barrier. In (NCCN)₂ the rotational spectrum appears to be perturbed by a low-frequency bending vibration, probably the vibration associated with the inversion tunnelling observed in (HCCH)₂. NH₃-NCCN has a dipole moment of 1.96D with a 3.063Å distance between the bonded nitrogen and the cyanogen center-of-mass. In (NCCN)₂ this distance is 3.142Å and the dipole moment 0.420D.

Address of Suni, Lee, and Klemperer: Dept. of Chemistry, Harvard University, Cambridge, MA 02138.

TF1 (1:30)

PURE ROTATIONAL TRANSITIONS IN SOLID PARA HYDROGEN

T. Byers and T. Oka

High resolution infrared spectroscopy of pure rotational and rovibrational transitions in solid hydrogen has become an area of increasing experimental and theoretical interest in our laboratory. In particular, the tetrahexapole induced $\Delta J=6$ pure rotational transition in solid para hydrogen has been observed to consist of three components¹ as a result of the interaction of the molecule with the crystal environment.²

In order to understand the observed spectrum and to plan future experiments to search for other possible transitions, we use the first principles theory developed by Van Kranendonk³ and others to calculate the expected splitting of an arbitrary rotational level and the intensities of the corresponding transitions. We extend the previous calculation by including higher multipole moments and higher order effects. Such a calculation is relevant in view of the high resolution and high sensitivity attainable by laser spectroscopy.

¹M. Okamura, M.-C. Chan, T. Oka, *Phys. Rev. Lett.* **62**, 32 (1989).

²M.-C. Chan, T. Oka, to be published.

³J. Van Kranendonk, *Solid Hydrogen*, Plenum Press, New York, 1983

Address of Byers and Oka: Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, IL 60637-1403

TF2 (1:47)

CRYSTAL FIELD SPLITTING OF THE $\Delta J = 6$ PURE ROTATIONAL $W_0(0)$ TRANSITION OF SOLID HYDROGEN: THEORY AND OBSERVATION

MAN-CHOR CHAN AND TAKESHI OKA

The pure rotational W ($\Delta J = 6$) transition of solid parahydrogen has been studied using high resolution difference frequency spectroscopy. In addition to the sharp feature reported in the previous work,¹ two new peaks were observed. This triplet structure agrees with the prediction from group theory.² These features were interpreted as the M levels in the $J = 6$ state split by crystal field interactions, based on the fact that the relative intensities of these components vary depending on the polarization of infrared source. Unlike the $J = 2$ roton, whose M splitting was interpreted by the roton hopping model of Van Kranendonk,³ the $J = 6$ roton is relatively localized based on an order of magnitude estimation of the hopping Hamiltonian. The observed splitting of $\sim 0.01 \text{ cm}^{-1}$ was therefore explained by the anisotropic induction and dispersion interactions of a localized $J = 6$ roton with the surrounding $J = 0$ molecules using the same treatment as the case of the crystal field effect of a localized $J = 1$ molecule in an otherwise $J = 0$ solid.⁴ The M value of each component was assigned according to intensity⁵ and energy calculations. The assignments, crystal field splitting, and spectral linewidth will be discussed following this idea.

¹M. Okumura, M.-C. Chan, and T. Oka, *Phys. Rev. Lett.* **62**, 32 (1989).

²R. E. Miller and J. C. Decus, *J. Chem. Phys.* **59**, 4871 (1973).

³J. Van Kranendonk, *Physica* **25**, 1180 (1959); J. Van Kranendonk, *Can. J. Phys.* **38**, 240 (1960).

⁴S. Luryi and J. Van Kranendonk, *Can. J. Phys.* **57**, 933 (1979).

⁵T. K. Balasubramanian, R. D'Souza, R. D'Cunha, and K. N. Rao, *Can. J. Phys.* **67**, 79 (1989).

Address of Chan and Oka: Department of Chemistry and Department of Astronomy and Astrophysics, the University of Chicago, Chicago, IL 60637.

TF3 (2:04)

ANALYSIS OF THE NEAREST NEIGHBORING (*nn*) *o*-H₂ PAIR TRANSITIONS IN THE FUNDAMENTAL *Q*-BRANCH OF SOLID HYDROGEN: GROUP THEORY AND INTENSITY CALCULATIONS

MAN-CHOR CHAN AND TAKESHI OKA

A rich spectrum composed of hundreds of transitions with typical linewidth of ~20 MHz has recently been observed¹ in the fundamental *Q* branch of solid *p*-H₂ (containing ~0.2% *o*-H₂) using high resolution difference frequency infrared laser spectroscopy. These features have been ascribed to the anisotropic electrostatic quadrupole-quadrupole and crystal field splitting of the vibrational transition of a pair of interacting *o*-H₂ molecules. While we are far from good understanding of the rich spectrum, attempts have been made to assign the transitions due to *nn* pairs of *o*-H₂, based on group theoretical considerations, and the observed frequencies and intensities. The symmetry group of an *nn* pair has been constructed by extending the group theory of matrix isolated molecule developed by Miller and Decius.² The transition intensities due to four different mechanisms were calculated based on the earlier theoretical studies of Harris, Berlinsky, and Hardy.³ A discussion on the detailed analysis based on symmetry considerations, intensities calculations, and the new observations of the dependence of polarization of the infrared radiation on the intensities will be presented.

¹M.-C. Chan, M. Okumura, C. M. Gabrys, L.-W. Xu, B. D. Rehfuss, and T. Oka, submitted to Phys. Rev. Lett.

²R. E. Miller and J. C. Decius, J. Chem. Phys. **59**, 4871 (1973).

³A. B. Harris, A. J. Berlinsky, and W. N. Hardy, Can. J. Phys. **55**, 1180 (1977).

Address of Chan and Oka: Department of Chemistry and Department of Astronomy and Astrophysics, the University of Chicago, Chicago, IL 60637.

TF4 (2:21)

DYE LASER SPECTROSCOPY OF MOLECULAR HYDROGEN

DAVID FERGUSON, K. NARAHARI RAO, LEE LARSEN, and M. E. MICKELSON.

The H₂ 4-0 S(1) and S(0) lines have been measured at various pressures in the range 200 Torr to 3000 Torr, using a ring dye laser, at an optical path of 5.984 kilometers. Initial analysis shows a possible non-linear density ("pressure") shift of the 4-0 S(1) line at low densities; this is in contrast to the usual straight line extrapolation¹⁻³. The experimental set-up also revealed an interesting interference effect in White-type multiple path absorption cells. A new method for multiple beam injection in a White cell will also be described. A measurement of the 5-0 S(1) line is being attempted.

¹A.R.W. McKellar, "The Significance of Pressure Shifts for the Interpretation of H₂ Quadrupole Lines in Planetary Spectra", ICARUS **22**, 212-219 (1974).

²Susan Lynn Bragg, "An Experimental Study of the Vibrational-Rotational Spectrum of Molecular Hydrogen", Ph.D. Dissertation, Washington University (1981).

³K. Narahari Rao, M. E. Mickelson, and J. T. Trauger, J. Mol. Structure, **217**, 85-98 (1990).

Address of Ferguson and Rao: Department of Physics, The Ohio State University, Columbus, Ohio, 43210.

Address of Larsen and Mickelson: Department of Physics and Astronomy, Denison University, Granville, Ohio, 43023.

TF5 (2:38)

INDUCED INFRARED ABSORPTION SPECTRA OF THE DOUBLE TRANSITIONS H_2 ($v=0 \rightarrow 1$) + D_2 ($v=0 \rightarrow 1$)

C. T. W. HSIEH and S. PADDI REDDY

Collision-induced infrared absorption spectra of the double transitions of H_2 ($v=0 \rightarrow 1$) and D_2 ($v=0 \rightarrow 1$) have been observed at 77 K and 201 K for the first time in the spectral region 7000 - 8000 cm^{-1} . The spectra were recorded with a 2 m absorption cell for total gas densities up to 550 amagat with partial gas density ratio of 1:1 of H_2 and D_2 at both temperatures. The observed transitions at 77 K, for example, are interpreted in terms of the following transitions:

Q_1 (1,0) of H_2 + Q_1 (2,1,0) of D_2 ,
 Q_1 (1,0) of H_2 + S_1 (0) of D_2 ,
 Q_1 (1,0) of H_2 + S_1 (1) of D_2 ,
 S_1 (0) of H_2 + Q_1 (2,1,0) of D_2 , and
 S_1 (1) of H_2 + Q_1 (2,1,0) of D_2 .

Analysis of the experimental absorption profiles will be presented using two different line shapes proposed in recent literature. The absorption coefficients, line-shape parameters, etc., obtained from the analysis will be also presented. The present spectra of H_2 + D_2 will be compared with those obtained for H_2 at 77 K and D_2 at 77 K in their first overtone regions and the arising problems will be discussed.

Address: Department of Physics, Memorial University of Nfld, St. John's, Nfld, CANADA, A1B 3X7

Intermission

TF'1 (3:05)

ANALYSIS OF THE $5_0^1, 6_0^1, 8_0^1$ AND 9_0^1 BANDS OF CH_2DF

W. Lewis-Bevan, D.F. Eggers, W.D. Stork and M.C.L. Gerry.

In a previous paper,¹ Lewis-Bevan et al. outlined the assignment and analysis of the two stronger fundamentals of CH_2DF in the 9-11 μm region, v_5 and v_6 , together with weaker v_9 fundamental. At that time it was suggested that the inclusion of v_8 would aid in the analysis of the data. In this paper we report the progress of the analysis of the four fundamentals. The data were re-recorded using both a high resolution BOMEM DA3.002 FT-IR instrument and a tunable diode laser. The diode laser was used to improve the resolution, sensitivity, and signal to noise of the very weak 1Q -branches of the v_9 fundamental, first observed in the FT-IR spectrum.

The analysis has been extended to include the strong v_8 fundamental. Molecular constants will be reported for the ground state and all four excited vibrational states of the molecule.

¹ W. Lewis-Bevan, D.F. Eggers, W.D. Stork and M.C.L. Gerry, Paper MF7 at the Forty-Fifth Symposium on Molecular Spectroscopy, June 11-15, 1990.

Address of Lewis-Bevan and Stork: Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901-4409.

Address of Eggers: Department of Chemistry BG-10, University of Washington, Seattle WA 98195.

Address of Gerry: Department of Chemistry, University of British Columbia, Vancouver, B.C. V6T 1Y6, Canada.

TF'2 (3:17)

INFRARED DIODE LASER SPECTROSCOPY OF FORMYL CHLORIDE: THE ν_6 BAND

Don E. Kristiansen and W. Lewis-Bevan

Formyl chloride is an unstable compound with a half life of approximately 30 minutes. The molecule has been observed in the reaction of ozone with chlorinated hydrocarbons. In this study, formyl chloride was prepared by the method of Takeo and Matsumura,¹ in which formic acid was passed over PCl_5 at room temperature. Based upon low resolution studies,² the ν_6 band at 932.3 cm^{-1} (H-C out-of-plane bend) should be perturbed, presumably by a Coriolis interaction with the ν_4 fundamental (C-Cl stretch) which is a very intense perpendicular band at 739 cm^{-1} . The ν_6 band, which is a pure C-type band, is very weak and lends itself to study under the high S/N of the diode laser. The results of the analysis and assignment will be discussed.

¹ H. Takeo and C. Matsumura, *J. Chem. Phys.* **64**, 4536 (1976)

² I.C. Hisatsune and J. Heicklen, *Canad. J. Spectrosc.* **18**, 77 (1973).

Address of Kristiansen and Lewis-Bevan: Dept. of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901-4409

TF'3 (3:29)

ANALYSIS OF THE CORIOLIS COUPLED 4_1^1 AND 6_1^1 BANDS OF DBF_2

W. D. Stork and W. Lewis-Bevan

A previous study on the normal species, HBF_2 ,¹ indirectly estimated the position of the unseen in-plane bending fundamental, ν_6 via a small Coriolis perturbation. In an attempt to observe this fundamental directly, the deuterated analogue, DBF_2 , was prepared *in situ* and its infrared absorption spectrum was recorded between 700 and 920 cm^{-1} using a high resolution Bomem DA3.002 FT-IR instrument. The strongest band in this region is the D-B out-of-plane bending fundamental, ν_4 . This type-C band is heavily perturbed via a Coriolis interaction. The nature of the perturbation has been established together with the assignment of transitions from the very weak type-A, D-B in-plane bending fundamental, ν_6 , the other fundamental involved in the perturbation.

The results of the assignments for both the ν_4 and ν_6 bands will be discussed, including the evaluation of ground and upper state rotational constants for both D^{11}BF_2 and D^{10}BF_2 . The nature of some observed perturbations will also be discussed.

¹ M.C.L. Gerry, W. Lewis-Bevan, D.J. MacLennan, A.J. Merer, and N.P.C. Westwood, *J. Mol. Spectrosc.* **98**, 143 (1986)

Address of Stork and Lewis-Bevan: Dept. of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901-4409

TF'4 (3:41)

AB INITIO CALCULATION OF VIBRATIONAL ABSORPTION AND CIRCULAR DICHROISM SPECTRA USING MP2 FORCE FIELDS: ASSIGNMENT OF THE VIBRATIONAL SPECTRA OF 2-OXETANONE, 4-METHYL AND 3-METHYL-2-OXETANONE

C. CHABALOWSKI, K.J. JALKANEN, F.J. DEVLIN AND P.J. STEPHENS

The vibrational absorption spectra of 2-oxetanone, and its 4- and 3-methyl derivatives and the vibrational circular dichroism (VCD) spectra of 4- and 3-methyl-2-oxetanone are predicted using harmonic force fields calculated at the MP2 level of approximation. The results are compared with the predictions of SCF harmonic force fields and with available experimental data. The spectra calculated using 6-31G* and 6-31G** MP2 force fields lead to nearly unambiguous assignment of the experimental spectra of 2-oxetanone, 4-methyl-2-oxetanone and 3-methyl-2-oxetanone.

Address for Chabalowski: U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD 21005-5066.

Address for Jalkanen, Devlin and Stephens: Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482.

TF'5 (3:58)

AB INITIO CALCULATION OF VIBRATIONAL ABSORPTION AND CIRCULAR DICHROISM SPECTRA USING MP2 FORCE FIELDS: CONFORMATIONAL ANALYSIS OF METHYL GLYCOLATE AND METHYL LACTATE

R. B. BURS, F.J. DEVLIN, C. CHABALOWSKI AND P.J. STEPHENS

The vibrational absorption spectra of methyl glycolate and lactate and the vibrational circular dichroism (VCD) spectrum of methyl lactate are predicted for several conformers of each molecule using harmonic force fields calculated at the MP2 level of approximation. The results are compared with available experimental spectra. The spectra calculated using 6-31G* or 6-31G** MP2 force fields permit the dominant solution conformers of methyl glycolate and lactate to be unambiguously identified.

Address for Burs, Devlin and Stephens: Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482.

Address for Chabalowski: U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD 21005-5066.

TF'6 (4:15)

FORMALISM FOR THE CALCULATION OF ATOMIC POLAR AND AXIAL TENSORS USING LOCALIZED MOLECULAR ORBITALS

I.D. BOUMAN, A.E. HANSEN AND P.J. STEPHENS

Expressions for atomic polar and axial tensors are derived via the Random Phase Approximation (RPA) permitting the use of non-canonical molecular orbitals, including localized molecular orbitals. In the case of the atomic axial tensors, these expressions permit the use of different gauge origins for individual molecular orbitals. Specific expressions resulting from the Local Origin Gauge (LORG) of Hansen and Bouman are presented. The Localized Molecular Orbital algorithm of Nafie and coworkers for atomic axial tensors is shown to be an approximation to the LORG expression.

An efficient methodology for the calculation of atomic polar and axial tensors using localized molecular orbitals has been implemented within the RPAC program. Preliminary results obtained for several small molecules will be presented.

Address for Bouman: Department of Chemistry, Southern Illinois University, Edwardsville, IL 62026

Address for Hansen: Department of Physical Chemistry, H.C. Ørsted Institute, DK-2100 Copenhagen Ø, Denmark

Address for Stephens: Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482

TF'7 (4:32)

MODELLING THE POTENTIAL ENERGY HYPERSURFACE OF THE HYDROGEN BOND HCN--HF

A. Quinones, G. Bandarage, R. R. Lucchese and J. W. Bevan

Initial modelling of the intermolecular potential hypersurface of the hydrogen bond dimer HCN--HF is reported. Extensive experimental rovibrational data associated with dimer fundamentals, overtones and combination bands allowed us to obtain a pseudo-triatomic intermolecular potential after averaging over vibrations involving the HCN fragment. This inverted potential was tested by a variational calculation of the bound states. The experimental results used in the inversion are reproduced to high accuracy. Ab-initio potential energy surfaces(MP2, TZ2P) were calculated for similar a model, and the bound states evaluated using the same variational calculation. A comparison of these results will be presented.

Chemistry Department, Texas A&M University, College Station, Texas 77843

TF'8 (4:49)

INVESTIGATION OF RELATIVISTIC EFFECTS IN HYDROGEN BOND INTERACTIONS: OC--HI

A. Suckley[†], Z. Wang^{*}, G. Bandarage^{*}, R. R. Lucchese^{*},
A. C. Legon[†], and J. W. Bevan^{*}

The hydrogen bond OC--HI has been characterized by high resolution microwave and infrared spectroscopies in supersonic seeded molecular jets. Ground state molecular parameters determined by microwave pulse-1 FTIR supersonic jet techniques include:

$$\begin{aligned} B_0 \text{ (MHz)} &= 900.9522(1) & D_J \text{ (kHz)} &= 2.519(1) \\ C_N \text{ (kHz)} &= 0.94(18) \\ \chi \text{ (MHz)} &= -1346.238(13) & \chi_J \text{ (kHz)} &= -8.27(31) \end{aligned}$$

and derived quantities:

$r(\text{C--I}) = 4.285\text{\AA}$ $\alpha = 24.8^\circ$ $k_\sigma(\text{Nm}^{-1}) = 1.71$ can be estimated from these analyses.

Infrared diode laser investigations provide a band origin frequency ν_0 of ν_2 C=O stretching vibration at $2148.549040(29) \text{ cm}^{-1}$ corresponding to a blue shift of $5.27728(37) \text{ cm}^{-1}$ relative to free monomer CO. Excited state $B_2 = 898.2728(33) \text{ MHz}$. and $D_J^{(2)} = 2.614(24) \text{ kHz}$. are evaluate... Experimental results and ab-initio calculations are used to investigate the influence of relativistic effects in this complex.

*Chemistry Department, Texas A&M University, College Station, Texas 77843

†Christopher Ingold Laboratories, Chemistry Department, University College, London, London WC1 HOAJ, U.K.

TG1 (1:30)

Radiative Transition Probabilities for all Vibrational Levels in the $X^1\Sigma^+$ State of HF

Warren T. Zemke, William C. Stwalley, Stephen R. Langhoff, G. L. Valderrama and Michael J. Berry

With the complete potential energy curve and dipole moment function at all internuclear distances R , the calculation of dipole moment matrix elements is possible for any vibration-rotation transition desired.

We use an improved potential energy curve for the $X^1\Sigma^+$ state of HF. It is based on the spectroscopically-determined potential of Coxon and Hajigeorgiou¹ plus the proper long-range behavior determined by including both dispersion and exchange effects.² The dipole moment function of this work is obtained from CASSCF/MRCI calculations for all R .

We report dipole moment absorption matrix elements and Einstein A spontaneous emission coefficients for the vibration-rotation bands within the $X^1\Sigma^+$ state of HF for all $v = 0 - 19$ observed levels and the $v = 20$ unobserved level.

¹ J. A. Coxon and P. G. Hajigeorgiou, *J. Mol. Spectrosc.* **142**, 254 (1990).

² W. T. Zemke, W. C. Stwalley, J. A. Coxon and P. G. Hajigeorgiou, *Chem. Phys. Lett.* **177**, 412 (1991).

Address of Zemke: Department of Chemistry, Wartburg College, Waverly, IA 50677

Address of Stwalley: Center for Laser Science and Engineering, and Departments of Chemistry and Physics, University of Iowa, Iowa City, IA 52242.

Address of Langhoff: Ames Research Center, NASA, Moffett Field, CA 94035

Address of Valderrama and Berry: Laser Applications Research Center, Houston Area Research Center, 4800 Research Forest Drive, The Woodlands, TX 77381 and Department of Chemistry, Rice University, Houston, TX 77251

TG2 (1:47)

THE MANY-LINE SPECTRA OF OH AND OD NEAR 1850 Å.

J.A. COXON, F. HOLLAND, AND K.P. HUBER.

We have observed the complex VUV spectra of OH and OD near 1850 Å¹ in emission from a corona discharge through supersonically expanding mixtures of H₂O or D₂O with He or Ar. The emission is particularly strong in the presence of He; under these conditions the spectrum produced with D₂O completely changes in character and reveals a regular lower-state progression of red-shaded bands. They arise in transitions from a single $^2\Pi_1$ vibronic level near $C^2\Sigma^+$ to $v''=13...18$ of the $X^2\Pi_1$ ground state of OD, extending the observations of the ground state potential to within 2350 cm⁻¹ of the $^3P + ^2S$ dissociation limit and providing the first experimental evidence for an excited $^2\Pi$ state of the hydroxyl radical. In all probability the spectra represent the strongest of several $^2\Pi - ^2\Pi$ transitions predicted by van Dishoeck et al.,² the radiative behavior of the loosely bound upper state being strongly influenced by overlapping Rydberg states of the same symmetry and by the unstable $^2\Pi$ state from $^1D + ^2S$ dissociation products.

¹ A. Michel, *Z. Naturforschg.* **12 a**, 887 (1957); P. Felenbock and J. Czarny, *Ann. Astrophys.* **27**, 244 (1964).

² E.F. van Dishoeck and A. Dalgarno, *J. Chem. Phys.* **79**, 873 (1983); E.F. van Dishoeck, M.C. van Hemert, A.C. Allison, and A. Dalgarno, *J. Chem. Phys.* **81**, 5709 (1984).

Address of Coxon: Dept. of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3.

Address of Holland: Forschungszentrum Julich GmbH, Inst. für Atmosphärische Chemie, D-5170 Julich, Germany.

Address of Huber: Herzberg Inst. of Astrophysics, National Research Council, Ottawa, Ontario, Canada K1A 0R6.

TG3 (2:04)

J-DEPENDENT LIFETIMES OF $\text{NO}(\text{B}^2\Pi)_{v=7}^*$

G. E. GADD, D. L. HUESTIS, AND T. G. SLANGER

Homogeneous interaction between the Rydberg $\text{C}^2\Pi$ and valence $\text{B}^2\Pi$ states of NO leads to both interesting spectroscopy and difficult interpretation of radiative properties, made more complicated by predissociation.

We have performed rotationally resolved LIF studies of the radiative properties of the $v=7$ vibrational level of the $\text{B}^2\Pi$ state of NO from $J=0.5$ to $J=17.5$. Three types of data were obtained: (1) fluorescence-excitation spectra to investigate the rotational dependence of bands in the B-X 7- v'' progression, (2) dispersed fluorescence spectra from excitation of specific J levels, and (3) radiative lifetimes as functions of J .

The $\Omega=1/2$ sublevels of the B(7) state lie 30 cm^{-1} or more below C(0,J). They have lifetimes in the range 200 to 700 ns, with a modest decrease as the dissociation limit is crossed at $J=7.5$. The J -dependence of the lifetimes and of the excitation and fluorescence spectra illustrate the influence of distant interaction with the C-state (see our previous study¹ of the lower $v=0-6$ levels).

The $\Omega=3/2$ sublevels of B(7), which intersect the two Ω components of C(0) near $J=2.5-4.5$, have much shorter decay lifetimes for low J values, about 40 ns, due to strong localized interaction with C(0). The decay rate decreases rapidly as J increases, merging with the values obtained for $\Omega=1/2$ by $J=10.5$.

*Research supported by NSF

¹G. E. Gadd and T. G. Slanger, J. Chem. Phys. 92, 2194 (1990).

Address of Huestis and Slanger: Molecular Physics Laboratory, SRI International, Menlo Park, CA 94025

Current address of Gadd: CSIRO Div. of Appl. Phys., Lindfield NSW 2070, Australia

TG4 (2:21)

HYPERFINE STRUCTURE MEASUREMENTS IN THE $\text{A}^3\Pi(1) \leftarrow \text{X}^1\Sigma^+$ ELECTRONIC TRANSITION OF I^{35}Cl NEAR THE DISSOCIATION LIMIT.¹

T. J. SLOTTERRACK, J. R. JOHNSON, K. C. JANDA, D. W. PRATT and C. M. WESTERN

Vibrational levels near the dissociation limit of the $\text{A}^3\Pi(1)$ electronic state of I^{35}Cl have been studied using fluorescence excitation techniques. By using a single mode ultra high resolution ring laser and a well collimated molecular beam, the hyperfine structure due to both the Iodine ($I = 5/2$) and Chlorine ($I = 3/2$) nuclei have been resolved. Calculation of the high energy vibrational wavefunctions, using a R.K.R level of theory, indicates that a large portion of a vibrational period is spent by the two nuclei at internuclear separations greater than their total van der Waals radii. This observation will be the basis for a discussion of the observed trends in the molecular electronic quadrupole (eQq_0 and eQq_2) and magnetic hyperfine (a) constants in terms of the atomic orientations as a function of internuclear separation.

¹Work supported by NSF.

Address of Slotterback, Janda, and Pratt: Department of Chemistry, University of Pittsburgh, Pittsburgh, Pa. 15260.

Address of Western: Department of Chemistry, University of Bristol, United Kingdom.

Address of Johnson: Thompson Electronics, Dallas, TX.

TG5 (2:38)

OBSERVATION AND ANALYSIS OF ION-PAIR TRANSITIONS OF I_2 IN A FREE-JET EXPANSION.

J. Tellinghuisen, X. Zhang, S. Fei, and M. C. Heaven.

The A' state of I_2 was observed for the first time in a free-jet expansion, where it was prepared by ArF laser excitation of I_2/Ar mixtures close to the nozzle¹. Twenty seven bands in the $v'' = 0$ progression of the $D' - A'$ transition were studied by laser excitation spectroscopy, leading to the following improved constants (cm^{-1}) for the A' and D' states:

$$B_0' = 0.028054, B_0'' = 0.020526, \alpha_0' = 5.3 \times 10^{-5}, \\ \omega_0' = 103.953, \omega_0 x_0' = 0.2097, \omega_0 y_0' = 2.687 \times 10^{-4}.$$

Many bands of the $\beta - A$ transition have also been observed. These originate from $A, v'' = 0$, and terminate on levels with $25 \leq v' \leq 68$ of the β state. Full analyses of both band systems will be presented.

1. J. Tellinghuisen, S. Fei, X. Zheng, and M. C. Heaven, Chem. Phys. Lett. **178**, 373 (1991).

Address of Tellinghuisen: Department of Chemistry, Vanderbilt University, Nashville, TN 37235.

Address of Zhang, Fei, and Heaven: Department of Chemistry, Emory University, Atlanta, GA 30322.

TG6 (2:55)

LASER INDUCED FLUORESCENCE SPECTRUM OF BiF ($A-X$)

MATTHEW BOHN, CHRIS BERST, AND ERNEST A. DORKO

A flow tube apparatus employing a high energy discharge has recently been fabricated to allow the production and observation of thermodynamically unstable materials. A high voltage discharge has been passed through a mixture of trimethyl bismuth (TMB) and sulfur hexafluoride (SF_6) to produce ground state $BiF(X)$. From the spectrally resolved chemiluminescence, bands characteristic of the BiF ($A-X$ 1-0, 2-5, 3-1, 4-2) transitions were observed in the region 4250-4750Å. Laser induced fluorescence (LIF) spectra of the ($A-X$) transitions were obtained with the use of an excimer pumped dye laser (using Stilbene-3 dye). Initial LIF measurements were made using a laser line width of 0.2 cm^{-1} . A comparison of the experimentally determined spectrum with a synthetic spectrum calculated using the constants of Jones and McLean¹ indicated that the ($A-X$ 1-0) transition of BiF was being excited. The intensity of the LIF was studied as a function of reagent gas pressures and delay times between the high voltage arc and the laser pulse. Rotational temperature measurements were made using an etalon which reduced the laser linewidth to 0.04 cm^{-1} . Twenty shots were averaged per data point and a total of 1000 data points were taken for the (1-0) transition. The rotational lines were found to be in Boltzmann equilibrium with rotational temperatures near 400K. Rovibronic constants calculated from the LIF measurements will be reported and discussed.

¹W.E. Jones and T.D. McLean, J. Mol. Spectrosc. **90** 481 (1981)

ADDRESS: PL/ARDJ, PHILLIPS LABORATORY, KIRTLAND AF BASE, NM 87117-6008

Intermission

TG7 (3:25)

HIGH RESOLUTION FOURIER TRANSFORM SPECTROSCOPY OF SUPERSONICALLY COOLED CN RADICAL

Brent. D. Reh fuss, M. H. Suh, Terry. A. Miller and V. E. Bondybey

We have recently acquired a high resolution Fourier transform spectrometer with the primary interest of studying molecular emission spectra, particularly in the infrared region. If one wished to design a molecule for testing and optimizing the performance of a spectrometer over a wide spectral region, one could hardly conceive of a better one than the CN radical. CN is probably the most studied diatomic free radical, and its properties have been previously investigated, including a recent observation by Vaida and co-workers.¹

The CN radical was produced in a corona discharge of acetonitrile entrained in an inert carrier gas, argon or helium, and expanded through a 0.2 mm nozzle. Stagnation pressures of 10 - 20 psi were used. Under these conditions the pressures in the chamber during operation were about 0.5 - 1 Torr. The nozzle was formed from a thick walled glass capillary, narrowed at one end to provide the desired size orifice. The anode consisted of a sharpened 2 mm diameter stainless steel wire. The metal tubing connecting the vacuum chamber to the pump, which was held at ground potential, served as the cathode. The anode was held at 3000 V with a discharge current of typically 4 - 5 mA.

Vibrational levels of the B - X transition have been observed up to $v = 14$ and rotational constants have been determined. The 0 - 0 transition shows evidence of a dual temperature, that most likely corresponds to two distinct formation mechanisms of the electronically excited B state molecules. Vibrational levels of the A - X transition have also been observed up to $v = 16$ and the $\Delta v = -1, -2$, and -3 bands extend well into the near IR down to 3000 cm^{-1} . Attempts to observe the X state vibrational emission are ongoing.

¹ E. C. Richard, D. J. Donaldson and V. Vaida, Chem. Phys. Lett. 157, 295 (1989).

Address of Reh fuss, Suh and Miller: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

Address of Bondybey: Institut für Physikalische Chemie der Technischen Universität, München, 8046 Garching, Germany.

TG8 (3:42)

MICROWAVE SPECTROSCOPY OF THE $v=3-10$ LEVELS OF $\text{CN}(X^2\Sigma^+)$

H. Ito, S. Yamamoto, S. Saito, and K. Kuchitsu

The fine structure and hyperfine coupling constants were determined by an analysis of the microwave spectrum of the $^{12}\text{CN}(X^2\Sigma^+)$, $v=3-10$ levels. For example, those for the $v=10$ level were determined as follows (in MHz):

$B=51385.864(10)$, $D=0.19606$ (fixed), $Y=156.777(14)$, $b=-25.841(66)$, $c=60.70(21)$, and $eQq=-0.171(68)$, where values in parentheses denote the standard errors.

The analysis of the spin-rotation constants, together with the reported values for the $^{13}\text{CN}(X^2\Sigma^+)$, $v=0-9$ levels,¹ showed that the second-order perturbation approximation was insufficient for the $^{12}\text{CN}(X^2\Sigma^+)$, $v=5-10$ levels. The electronic structure of the $\text{CN}(X^2\Sigma^+)$ state was studied on the basis of an analysis of the vibrational dependence of the hyperfine constants, where the free atom comparison method was found to be insufficient.

¹ M. Bogey, C. Demuynck, and J.L. Destombes, Chem. Phys. Lett. 102, 141 (1986).

Address of Ito and Kuchitsu: Department of Chemistry, Nagaoka University of Technology, Nagaoka 940-21, Japan.

Address of Yamamoto and Saito: Department of Astrophysics, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464, Japan

TG9 (3:59)

PHOTOFRAGMENT SPECTROSCOPY OF CS₂ AT 206–200 nm

Caroline Starrs and John Hepburn

The photofragmentation of CS₂ in the region 206–200 nm has been studied under supersonic molecular beam conditions, with the S atom products being detected by vacuum ultraviolet laser-induced fluorescence. The excitation spectrum for the S(¹D₂) and S(³P₂) products can be measured by scanning the photolysis laser over the $\bar{B}^1\Sigma_u^+$ (¹B₂) ← X¹Σ_g⁺ absorption system. These spectra provide information on the spectroscopy and dynamics of the predissociating B state.

Address: Centre for Molecular Beams and Laser Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.

TG10 (4:16)

HIGH RESOLUTION SPECTROSCOPY OF Na₃ BY CW RESONANT TWO-PHOTON IONIZATION STEFAN RAKOWSKY AND WOLFGANG E. ERNST

Na clusters are generated in a seeded supersonic molecular beam. Na₃ molecules are resonantly excited by a cw single mode dye laser and subsequently ionized by a cw Argon ion laser. The Na₃⁺ signal is detected through a quadrupole mass spectrometer.

In this way, spectra of the B-X transition of Na₃ around 620 nm were recorded with linewidths of 0.1 to 1. GHz. The rotational transitions exhibit different hyperfine splittings which are resolved for part of the lines.

First results for the rotational constants from an analysis of the spectra with model Hamiltonians will be reported. In addition, we are setting up an optical-optical double resonance experiment in order to label several rotational transitions.

Address of authors: Dept. of Physics, The Pennsylvania State University, University Park, Pa. 16802

TG11 (4:28)

ROTATIONAL, FINE, AND HYPERFINE STRUCTURE OF Ar-OH VAN DER WAALS COMPLEX

Bor-Chen Chang, David W. Cullin, James M. Williamson, Lian Yu, Brent D. Reh fuss, and Terry A. Miller

Last year, we reported the observation of the rotationally resolved spectrum of Ar-OH.¹ In our spectrum, we also can observe the fine and hyperfine structure of Ar-OH, which is quite different from that of OH radical. We have finished the analysis of the rotational, fine, and hyperfine structure of the Ar-OH pure van der Waals stretch bands (A bands). The results show the electronic excited state of Ar-OH is a Hund's case (b)_{gs} rather than the Hund's case (b)_{g1} of OH. The Fermi contact constant and spin-rotation coupling constant of Ar-OH are 724(12) MHz and 28(12) MHz respectively. Compared to those parameters in OH, the Fermi contact constant of Ar-OH decreases by about 7%. On the other hand, the spin-rotation coupling constant of Ar-OH is about 10⁻³ of that of OH. The details of this analysis will be discussed.

¹B.-C. Chang, D. W. Cullin, J. M. Williamson, B. D. Reh fuss, L. Yu, and T. A. Miller, 45th Symposium on Molecular Spectroscopy, The Ohio State University, June 11-15, 1990, Columbus, Ohio, Paper TH 5

Address of Authors: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 West 18th Avenue, Columbus, Ohio 43210

TG12 (4:45)

FLUORESCENCE EXCITATION AND RESOLVED EMISSION SPECTRA OF SUPERSONICALLY COOLED Al_2O

Ming-Fang Cai, Christopher C. Carter, Terry A. Miller, and Vladimir E. Bondybey

The triatomic oxide, Al_2O , was prepared by oxidation of laser vaporized aluminum, or by vaporization of alumina. Both fluorescence excitation and wavelength resolved emission spectra were taken of a transition located near 38249 cm^{-1} . These spectra are consistent with a linear, centrosymmetric Al-O-Al structure. Analysis of the spectrum yields an AlO bond length of 0.164 nm and values of 525 cm^{-1} (Σ_g^+), 99 cm^{-1} (Π_u), and 992 cm^{-1} (Σ_g^+) for the ground state fundamental vibrations, which are in good agreement with theoretical values.

Address of Authors: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 West 18th Avenue, Columbus, OH 43210

Address of Bondybey: Institut für Physikalische Chemie, T. U. München 8046 Garching, Germany

TG13 (4:57)

LASER INDUCED FLUORESCENCE AND STIMULATED EMISSION PUMPING OF CD_2

Wei Xie and Hai-Lung Dai

Laser Induced Fluorescence (LIF) and Stimulated Emission Pumping (SEP) are used to characterize the CD_2 $\tilde{X}^1A_1 \longleftrightarrow \tilde{B}^1B_1$ rovibronic transitions. CD_2 is generated from photolysis of d_2 -ketene. Rotational constants and vibrational term values of both electronic states have been determined. Perturbations to the \tilde{X} state rotation-vibration level energies caused by singlet-triplet coupling appeared to be more prominent in CD_2 than in CH_2 . The ratio of the $\Delta K_v=3/\Delta K_v=1$ transition intensities is compared with the ones of the CH_2 transitions. This allows us to assess the importance of the Renner-Teller effect in inducing the abnormally strong $\Delta K_v=3$ transitions.

Address: Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323

WA1

STRATOSCOPY: THE INTER STELLAR CONNECTION. 35 min.

ERIC HERBST, Department of Physics, Duke University, Durham, North Carolina, 27706.

WA2

MODELING VIBRATION-ROTATION IN SPHERICAL TOP
MOLECULES: THEORY AND PRACTICE. 35 min.

J.P. CHAMPION, Laboratoire de Spectronomie Moleculaire et Instrumentation Laser,
Universite de Bourgogne, Dijon, France.

INTERMISSION

WA3

THEORETICAL ANALYSIS OF ROVIBRATIONAL STRUCTURE. QUANTUM
BIFURCATIONS AND CATASTROPHES.

B.I.ZHILINSKII

Review of recent studies on qualitative phenomena in excited
isolated molecules [1-4] will be given.

Modifications of energy spectra and intramolecular dynamics under
the variation of strict or approximate integrals of motion are
studied theoretically for different molecular problems. New types
of qualitative phenomena appropriate for the quantum systems with
a small number of degrees of freedom are predicted and classified
via simultaneous using of bifurcation (catastrophe) theory and
group theoretical approach.

Manifestation of quantum bifurcations (catastrophes) in high
resolution molecular spectra is discussed on different examples
of concrete molecules. The importance of the approach developed
for the prediction of the crucial points for further experimental
study is evidenced.

- [1] I.M.Pavlichenkov, B.I.Zhilinskii, Ann.Pays.184, 1 (1988)
- [2] B.I.Zhilinskii, Chem.Pays. 137, 1 (1989)
- [3] D.A.Sadovskii, B.I.Zhilinskii, J.P.Champion, G.Pierre,
J.Chem.Phys. 92, 1523 (1990)
- [4] V.M.Krivtsun, D.A.Sadovskii, B.I.Zhilinskii, J.Mol.Spectrosc.
139, 126 (1990)

Address of B.I.Zhilinskii: Chemistry Department, Moscow State
University, Moscow 119899 USSR

WA4

SPECTROSCOPY BY AB INITIO QUANTUM CHEMISTRY
NICHOLAS C. HANDY

It is now possible to calculate by analytic methods first, second, third and fourth derivatives of the Self
Consistent Field energy. It is also possible to calculate first and second derivatives of the MP2 energy, and the first
derivative of more sophisticated methods such as Coupled Cluster theory. We give evidence to recommend that MP2
(or CC) methods should be used for the quadratic force field and SCF for the anharmonic field.

We use second order perturbation theory to calculate the spectroscopic constants (with SPECTRO).
Applications will be reported.

Address: Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, England

WA5

TENTATIVE IDENTIFICATION OF $(H_2)_2$ DIMER EMISSION IN THE 2-MICRON AURORAL SPECTRUM OF JUPITER

L. M. TRAFTON AND J. K. G. WATSON.

The auroral emission spectrum of Jupiter is normally confined to small areas near the north and south poles, but on two occasions in September and November 1988 much more widespread activity was observed in the 2- μ m wavelength region. The lines observed in this global-scale activity are different from those of H_2 and H_3^+ in the normal auroral emission at this wavelength, and were different on the two different occasions in 1988. From comparisons with laboratory absorption spectra^{1,2}, it is suggested that these lines are due to the dimer $(H_2)_2$, observed in emission for the first time. The November 1988 lines have unstable upper levels with $l \geq 2$, while the September 1988 lines have bound upper levels with $l \leq 1$. The proposed explanation of these unusual relative intensities is that the November lines were formed by inverse predissociation $H_2^+ + H_2 \rightarrow [(H_2)_2]^* \rightarrow (H_2)_2 + h\nu$ at a level in the atmosphere where the pressure is sufficient to favor the two-body process over normal auroral quadrupole emission from the excited monomer H_2^+ , whereas the September lines were from a higher-pressure level which allows the three-body process $H_2^+ + H_2 + M \rightarrow (H_2)_2^* + M \rightarrow (H_2)_2 + h\nu + M$, where M is probably H_2 , to be dominant. This interpretation suggests that widespread auroral activity can be confined to different pressure levels on different occasions.

1. A. R. W. McKellar and H. L. Welsh, *Can. J. Phys.* **52**, 1082-1089 (1974).
2. A. R. W. McKellar, *J. Chem. Phys.* **92**, 3261-3277 (1990).

Address of Trafton: McDonald Observatory and Department of Astronomy, University of Texas at Austin, Austin, TX 78712.

Address of Watson: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.

WE1 (1:30)

CARBON CAGE RESEARCH AT RICE UNIVERSITY

R. E. Curl

An overview of research at Rice on carbon cage molecules will be presented. This research involves several different laboratories and over a dozen investigators. The emphasis will be placed on the spectroscopic and chemical physics results obtained, primarily in the laboratory of R. E. Smalley. In particular, molecular beam spectroscopies of C_{60} and C_{60}^+ are being investigated by resonance enhanced two photon ionization (R2PI), by photoelectron spectroscopy of C_{60}^- and by photofragmentation of van der Waals complexes of C_{60} and C_{60}^+ . It is found from the photoelectron spectrum of C_{60}^- and C_{70}^- that the lowest triplet states of C_{60} and C_{70} are about 1.7 and 1.6 eV above the ground singlet electronic state, respectively. By time-resolved R2PI probing, the lifetimes of these states, when prepared by 4.03 eV excitation, are 42 and 41 μ s for C_{60} and C_{70} respectively. The van der Waals complex, $C_{60}^+ \cdot Ar$ can be prepared in two different ways and exhibits remarkably different photofragmentation properties depending upon the method of preparation. Ongoing work is aimed at obtaining the electronic spectra of very cold C_{60} and C_{60}^+ by R2PI.

Address of Curl: Department of Chemistry, Rice University, Houston, TX 77251.

WE2 (2:03)

Ohio State University Symposium on Molecular Spectroscopy
June 17-21, 1991

Title:

From Interstellar Dust to Fullerenes

Author:

Wolfgang Krätschmer, Max-Planck-Institut für Kernphysik
PO Box 103980
D-6900 Heidelberg
Germany

Abstract:

During the work in which we attempted to simulate the strong interstellar 217 nm absorption by laboratory produced soot, we noticed UV absorptions which turned out to belong to fullerenes formed along with the soot. This discovery opened the way to produce the fullerene molecules C_{60} , C_{70} , and (with a much smaller yield) also larger species in gram quantities. As the most abundant fullerene we obtained the soccerball shaped C_{60} molecule. After extraction from the soot, the fullerenes can be prepared into various ways, e.g. in the form of vapour, amorphous coatings, or crystalline solids, and thus studied in much greater detail than was previously possible. A status report of our work on the UV and IR spectra of fullerenes will be given.

WE3 (2:36)

C₆₀ AND C₆₀M COMPLEXES; THEORETICAL TREATMENT OF ELECTRONIC STRUCTURE, IONIZATION POTENTIALS, AND EXCITATION ENERGIES

RUSSELL M. PITZER

Restricted Hartree-Fock *ab initio* calculations using relativistic core potentials were performed on C₆₀ and C₆₀M (M=K, Ca, Mn, Cs, Ba, La, Eu, U) complexes with M as the central metal atom. The icosahedral symmetry was used to great advantage in the calculations. The ground and excited states of both neutral complexes and their positive ions were studied, and the population analyses for the ground states of the complexes were obtained. The C₆₀ cage accepts one or two electrons from metal atoms in a formal sense, but the actual charge is usually less. Electrons in large-radius s orbitals on the metal atom tend to move outward to the carbon cage or inward to smaller-radius d orbitals on the metal atom. For the larger metal atoms, ionization occurs from a cage orbital so that the ionization potentials of these complexes are almost constant.

Coworkers: Agnes H. H. Chang and Walter C. Ermler

Address of Chang and Pitzer: Department of Chemistry, The Ohio State University, 120 West 18th Avenue, Columbus, OH 43210

Address of Ermler: Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, NJ 07030

Intermission

WE4 (3:20)

THE DISCOVERY OF C₆₀, THE THIRD FORM OF CARBON, AND ITS IMPLICATIONS FOR CHEMISTRY ON EARTH AND IN SPACE

H.W. KROTO

The apparent stability of C₆₀ Buckminsterfullerene was originally discovered during a study of the role of carbon chemistry in space and its spheroidal hollow cage structure has now been confirmed by some down-to-earth experiments in the laboratory. It is difficult to accept, but it appears that this third form of carbon has been forming spontaneously under our noses since time immemorial. It is the spontaneous creation of this most beautiful and elusive of species which has major implications for a deeper understanding of the chemical factors governing mechanism in organic chemistry, the morphology of graphitic materials and the composition of circumstellar shells and the interstellar medium. This exciting discovery, which promises major applications in the materials area, has its origins in a fundamental science programme which involved the detection of long carbon chain molecules in space by radioastronomy and the quest for an understanding of how they came to be there.

Address: School of Chemistry and Molecular Sciences, University of Sussex, Brighton, BN1 9QJ UK.

WE5 (3:53)**INFRARED EMISSION SPECTRUM OF GAS PHASE C_{60}** C.I. FRUM, R. ENGLEMAN JR., H.G. HEDDERICH, P.F. BERNATH, L.D. LAMB AND D.R. HUFFMAN

The gas phase infrared spectrum of C_{60} has been observed in emission with the National Solar Observatory Fourier transform spectrometer at Kitt Peak. Bands attributable to the C_{60} molecule are found at 527.1 cm^{-1} , 570.3 cm^{-1} , 1169.1 cm^{-1} and 1406.9 cm^{-1} . Additional emission features are tentatively assigned to C_{70} or combination bands of C_{60} . A new, strong emission is observed at 1010.2 cm^{-1} belonging to an unknown molecule. None of these features can be associated with any of the strong emission bands observed so far in astronomical sources.

Address of Frum, Engleman, Hedderich and Bernath: Department of Chemistry, University of Arizona, Tucson, Arizona, 85721 USA.

Address of Lamb and Huffman: Department of Physics, University of Arizona, Tucson, Arizona 85721 USA.

Current Address of Hedderich and Bernath: Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.

WE6 (4:26)**Observation of the Doubly Charged, Gas Phase Anion of Buckminsterfullerene, C_{60}^{2-}** P.A. Limbach, L.C. Schweikhard, K.A. Cowen, M.T. McDermott, A.G. Marshall, and J.V. Coe

The fullerenes exhibit a remarkable ability to accommodate excess negative charge. We have observed C_{60}^{2-} in a Fourier transform ion cyclotron resonance mass spectrometer by laser vaporization of raw fullerene material which had been extracted from soot produced with graphite rods. A variety of tests were performed to verify the existence of the double negatively charged species. The most definitive of these measures frequency shifts as a function of ICR trapping voltage.

Address: Department of Chemistry, the Ohio State University, Columbus OH 43210.

WE7 (4:38)**FAR INFRARED BENDING MODE FOR C_4 TRAPPED IN Ar ¹**P.A. WITHEY, L.N. SHEN, AND W.R.M. GRAHAM

The bending mode of the C_4 chain has been observed for the first time at 172.4 cm^{-1} in the Fourier transform spectrum of the vacuum ultraviolet photolysis products of 1,3-butadiene and acetylene trapped in Ar at 10 K. The assignment is confirmed by ^{13}C isotopic data; is consistent with the earlier identification² of the antisymmetric C-C stretching mode at 1543.4 cm^{-1} (found more recently in the gas phase³ at 1548.937 cm^{-1}); and is in agreement with the predictions of *ab initio* calculations.⁴

¹Supported by the W.M. Keck Foundation and the Welch Foundation (Grant P-0786).

²L.N. Shen and W.R.M. Graham, J. Chem. Phys. **91**, 5115 (1989).

³J.R. Heath and R.J. Sakally, J. Chem. Phys. **94**, 3271 (1991).

⁴D. Michalska, H. Chojnacki, B.A. Hess, and L.J. Schaad, Chem. Phys. Lett. **141**, 376 (1987).

Address of Withey and Graham: Department of Physics, Texas Christian University, Fort Worth, Texas, 76129.

Address of Shen: Chemical Engineering, Box 2159, Yale University, New Haven, Connecticut, 06520.

WE8 (4:55)

IS C₄ BENT?
D.W. EWING

Cheung and Graham have recently obtained high resolution ESR spectra of the C₄ molecule in rare gas matrices which show splitting of the perpendicular lines into separate x and y components.¹ Their interpretation of these spectra is that triplet C₄ is not linear, but is slightly bent. This is contrary to several recent *ab initio* calculations.

Using larger basis sets than have previously been employed for C₄, TZ2P and TZ2PF, the structure of this molecule has been reinvestigated via *ab initio* calculations which include electron correlation to second order in the many-body perturbation scheme. Linear, several forms of alinear, and rhombic C₄ were studied.

Within the levels of theory employed here, triplet C₄ is not bent, but rather is linear. The amount of energy required to bend linear C₄ is quite small, however. This may account for the molecule being slightly bent in a matrix. The inclusion of f functions in the basis set lowers the energy of rhombic C₄ about 10 kJ/mol more than that of linear C₄.

¹H.M. Cheung and W.R.M. Graham, J. Chem. Phys. **91**, 6664 (1989).

Address of Ewing: Department of Chemistry, John Carroll University, Cleveland, OH 44118.

WE9 (5:07)

Ab initio theoretical predictions of the equilibrium geometries of C₆₀, C₇₀, C₆₀H₈₀ and C₆₀F₈₀

Gustavo E. Scuseria

Department of Chemistry and Rice Quantum Institute,
 Rice University, Houston, Texas 77251-1892

The recent development of a technique to obtain C₆₀ in macroscopic quantity has originated a flurry of experiments confirming, among other things, the existence of the icosahedral soccer-ball structure for this form of elementary carbon proposed back in 1985. In this work,^a the equilibrium geometries and relative stabilities of the hypothetical C₆₀H₈₀ and C₆₀F₈₀ molecules are predicted at the self-consistent field (SCF) Hartree-Fock (HF) level of theory employing basis sets of double zeta plus polarization (DZP) quality. For C₆₀, the geometry was also optimized with a larger triple-zeta plus polarization (TZP) basis set. For C₆₀, the 1800 basis functions DZP geometry optimization is the largest *ab initio* Hartree-Fock analytic energy calculation reported to date. Results obtained in this work indicate that both C₆₀H₈₀ and C₆₀F₈₀ should be observable in the laboratory.

Ab initio SCF HF calculations employing basis sets of DZP quality are also reported for C₇₀. The D_{5h} rugby-ball shaped equilibrium geometry, obtained via analytic energy derivatives, is reminiscent of C₆₀ except for a ring of 10 carbon atoms that give rise to a central band of five hexagons composed of aromatic C-C bonds. The calculated ionization potential of C₇₀ (7.6 eV) is in excellent agreement with recent experimental measurements

^a G. E. Scuseria, Chem. Phys. Lett. **176**, 423 (1991).

WE10 (5:19)**EPR SPECTRA OF C₆₀ ANION AND CATION RADICALS****S. G. KUKOLICH AND D. R. HUFFMAN**

EPR spectra of anion and cation radicals produced from a nearly pure C₆₀ sample and samples containing C₆₀ and C₇₀ were recorded at 9.1 GHz. The measured g-value which is assigned to (C₆₀)⁺ is 2.003. Three different g-values near 2.000 for three different anion radicals of C₆₀ were observed. Linewidths were less than 0.5 gauss, with no apparent hyperfine structure for any of the ion radicals.

Address of Kukolich: Department of Chemistry, The University of Arizona, Tucson, Arizona, 85721

Address of Huffman: Department of Physics, The University of Arizona, Tucson, Arizona, 85721

WF1 (1:30)

COLLISIONAL LINE MIXING IN THE RQ_0 BRANCH OF THE ν_5 BAND OF CH_3Cl N. LACOME, L. R. BROWN, C. CHACKERIAN, JR. and G. TARRAGO

The RQ_0 transitions of the ν_5 band of CH_3Cl between 1459.5 and 1460.0 cm^{-1} show the effects of line mixing in the 0.005 cm^{-1} resolution spectra recorded with the FTS at Kitt Peak National Observatory/National Solar Observatory. The line mixing has been modelled in the self-broadened spectrum of methyl chloride using the MEG (Modified Exponential Gap) law for scaling inelastic rates. The effect, on the mixing, of different collisional selection rules has been investigated. The line positions, intensities and γ_{self} have been measured for the RQ_0 branch for $J = 0 - 37$ of $CH_3^{35}Cl$ using four low pressure (0.2 to 0.7 Torr) and four higher pressure (8 to 23 Torr) spectra. The accuracies are ± 0.0003 cm^{-1} for the positions, $\pm 3\%$ for intensities and $\pm 4\%$ for widths. The self-broadened line widths vary from 0.582 to 0.248 cm^{-1}/atm . These measurements have been used to validate the line parameters used in the calculations and to obtain the parameters in the MEG scaling law.

Address of Lacomé: Laboratoire de Spectrochimie Moléculaire, Université Pierre et Marie Curie, Bat. F., 4 Place Jussieu, 75252 Paris Cedex 05, France.

Address of Brown: Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, CA 91109, USA.

Address of Chackerian: NASA Ames Research Center, Moffett Field, CA 94035-1000, USA.

Address of Tarrago: L.P.M.A., Université de Paris-Sud, Bat 350, 91405 Orsay Cedex, France.

WF2 (1:47)

SELF-BROADENING AND LINE-MIXING IN HCN Q BRANCHES

A.S. PINE AND J.P. LOONEY

The Q branches of the $\nu_1 + \nu_2$ (4004 cm^{-1}) and $\nu_2 + \nu_3$ (2806 cm^{-1}) combination bands and the $\nu_1 - \nu_2$ (2599 cm^{-1}) difference hot band of HCN have been recorded at pressures from 1 to 400 Torr using a tunable difference-frequency laser. The self-broadening coefficients are identical for all three bands involving the ν_2 Π bending mode and are within experimental error of those reported previously for $\Sigma - \Sigma$ stretching bands. The J dependence of the self-broadening coefficients exhibits a maximum near the Boltzmann population peak and is well described by semiclassical line-broadening theory incorporating known measured or *ab initio* dipole and quadrupole moments, curved trajectories and an isotropic Lennard-Jones short-range potential. Line-mixing is evident from the non-additive Q-branch collapse when the spectral lines overlap due to pressure broadening, but the line coupling is reduced by the g-f cross-relaxation in the k -doubled Π bending vibration. However, the inelastic rotational collision rates required to fit the spectral line-mixing profiles are poorly represented by empirical exponential-energy-gap scaling laws for both R-T and R-R energy transfer.

Address: Molecular Physics Division (ASP) and Thermophysics Division (JPL), National Institute of Standards and Technology, Gaithersburg, MD 20899.

WF3 (2:04)

MEASUREMENTS OF COLLISIONAL WIDTHS OF H₂O FROM FOURIER TRANSFORM FLAME SPECTRA BETWEEN 800 AND 1800 CM⁻¹

V. DANA, J.-Y. MANDIN, C. CAMY-PEYRET, J.-M. FLAUD, AND L.S. ROTHMAN

The collisional widths of more than 400 transitions of the H₂O molecule have been measured using a Fourier transform spectrum of an air-methane flame at 2000 K.

Among these transitions, more than 360 belong to the $n\nu_2 - (n-1)\nu_2$ bands, and about 80 are purely rotational transitions.

The results show a strong decreasing of the collisional widths when the rotational quantum number J increases, as well as a non negligible decreasing of the collisional widths when the ν_2 vibrational quantum number increases.

Address of Dana, Mandin, Camy-Peyret, and Flaud: Laboratoire de Physique Moléculaire et Applications, CNRS et Université Pierre et Marie Curie, Bte 76, Tour 13, 4, place Jussieu, 75252 Paris cedex 05, France.

Address of Rothman: Department of the Air Force Geophysics Laboratory (AFSC), Optical Physics Division, Hanscom Air Force Base, MA 01731-5000, U.S.A.

WF4 (2:16)

N₂-BROADENING AND LINE SHIFTS IN THE ν_3 BAND OF CO₂ AND THE ν_2 BAND OF H₂O

V. MALATHY DEVI, D. CHRIS BENNER, MARY ANN H. SMITH AND CURTIS P. RINSLAND

On several of our spectra recorded with the McMath Fourier transform spectrometer (0.01-cm⁻¹ resolution) the ν_3 region of CO₂ and/or the ν_2 region of H₂O were obtained incidentally when neighboring spectral regions were being studied. Often the spectral lines of these gases were used for wavelength calibration of the spectra. The lines of these bands are extremely intense and arise from residual gas in the evacuated interferometer tank and the nitrogen-purged atmospheric path. We have analyzed a number of spectra in which overlapping pairs of lines appear from both of these sources. In many cases, a difference in the line center positions of the narrow and broad components is clearly visible. Measuring this position difference gives a direct determination of the pressure-induced line shift. For each pair of lines, the two positions and the N₂-broadened halfwidth of the broader component have been measured using a nonlinear least squares spectrum fitting algorithm.

For the ν_3 band of CO₂ the measurements were made in the P(40) to R(40) spectral range. The halfwidths range from 0.086 to 0.062 cm⁻¹/atm and vary smoothly with rotational quantum number within the uncertainties of the measurement (about 2%). P and R branch lines with the same J'' have similar halfwidths. Pressure-induced line shifts in the P branch are almost the same for all lines to the accuracy of the measurements (-0.0028 cm⁻¹/atm with uncertainties of 0.0002 cm⁻¹/atm). In the R branch, however, there is a strong dependence upon rotational quantum number, varying from a shift close to zero at $J''=2$ to a shift of -0.0032 cm⁻¹/atm near $J''=40$.

Over 100 spectral lines of H₂O were measured. The halfwidths varied from about 0.04 to 0.09 cm⁻¹/atm. Unlike our results for CO₂ or those obtained for CH₄ or O₃ in our previous studies, approximately equal numbers of positive and negative line shifts were found for the H₂O lines measured. The magnitude of the shift is typically a few thousandths of a cm⁻¹ per atmosphere.

Address of Malathy Devi and Benner: Department of Physics, College of William and Mary, Williamsburg, VA 23185.

Address of Smith and Rinsland: Atmospheric Sciences Division, NASA Langley Research Center, Mail Stop 401A, Hampton, VA 23665-5225.

WF5 (2:33)

LORENTZ BROADENING AND PRESSURE-INDUCED LINESHIFT COEFFICIENTS IN THE ν_2 BAND OF HD¹⁸O

C. P. RINSLAND, M. A. H. SMITH, V. MALATHY DEVI, AND D. C. BENNER

In the present work, we report measurements of Lorentz broadening coefficients and pressure-induced line shift coefficients for over 100 transitions in the ν_2 band of HD¹⁸O. Nitrogen, oxygen, and dry air have been used as the perturbing gases. The results were obtained by analyzing 13 room temperature laboratory absorption spectra recorded at 0.0053-cm⁻¹ resolution with the Fourier transform spectrometer in the McMath solar telescope on Kitt Peak. This instrument is operated by the National Solar Observatory. A signal-to-rms noise ratio of about 500 was achieved with a 40-minute integration time per spectrum.

A 1.21-m absorption path cell was used throughout the experiment. The samples were prepared by mixing distilled H₂O with 99.96 atom% D₂O. Different low pressure samples (at 1.0 Torr or less) were prepared with varying initial amounts of H₂O and D₂O. Spectra of three of these samples were analyzed to determine the unshifted line center positions. The HDO assignments were obtained from previous investigations.^{1,2} Interfering lines of H₂O and D₂O were also readily identified.^{1,3} For the broadening measurements, the low pressure HDO+H₂O+D₂O mixtures were diluted with high purity nitrogen, oxygen, or dry air. Spectra were recorded with total sample pressures of about 200, 300, and 400 Torr. The partial pressure of HDO was less than 0.2% in all cases. A nonlinear least-squares spectral fitting technique was used in the data analysis (see, for example, Rinsland et al.⁴). The wavenumber scale of each spectrum was calibrated with respect to the positions of the narrow (low pressure) component of strong, isolated ν_2 band H₂¹⁸O lines.

The dependence of the measured coefficients on the transition quantum numbers will be discussed. The measured values will also be compared with previous experimental determinations and the calculated parameters on the 1991 NITRAN line parameters compilation. Measurements have also been obtained for a number of lines of the D₂¹⁸O ν_2 band, and these results will be compared with the few experimental values in the literature.

Spectroscopic measurements of water vapor isotope ratios are a sensitive probe of the effects of methane oxidation on the hydrogen budget of the Earth's stratosphere. The significance of such work will be briefly reviewed.

¹L. R. Brown et al., *Appl. Opt.* **26**, 5154-5182 (1987).²J.-M. Flaud et al., *Int. J. Infrared and Millimeter Waves* **7**, 1063-1090 (1986).³G. Camy-Peyret et al., *Int. J. Infrared and Millimeter Waves* **6**, 199-233 (1985).⁴C. P. Rinsland et al. *Appl. Opt.* **27**, 631-651 (1988).

Address of Rinsland and Smith: Atmospheric Sciences Division, NASA Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665-5225.

Address of Malathy Devi and Benner: Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185.

WF6 (2:45)

NEW CALCULATIONS FOR WATER BY THE TECHNIQUE OF
DIRECT NUMERICAL DIAGONALIZATION*Richard B. Wattson and Gary E. Galica*

The direct numerical diagonalization (DND) method¹, which has achieved considerable success with calculations for CO₂, is now being applied to calculations of line position and intensity for the water molecule. The basis functions utilized by Johnson², the bisector valence coordinate Hamiltonian developed by Carter, Handy, and Sutcliffe³, and the potential function calculated by Jensen⁴ have been combined with the direct product expansion approach of DND. Comparisons will be given between Jensen's potential function, expanded around the equilibrium angle, and a preliminary potential function, expanded around linearity. Comparison of our calculations with previous investigators and observations will be given with respect to line intensity as well as line position data.

¹R. B. WATTSON AND L. S. ROTHMAN, *J. Mol. Spectrosc.* **119**, 83-100 (1986).²B. R. JOHNSON AND W. P. REINHARDT, *J. Chem. Phys.* **85**, 4538-4556 (1986).³S. CARTER, N. C. HANDY, AND B. T. SUTCLIFFE, *Mol. Phys.* **49**, 745-748 (1983).⁴P. JENSEN, *J. Mol. Spectrosc.* **133**, 438-460 (1989).

Address of Wattson and Galica: Visidyne, Inc., 10 Corporate Pl., S. Bedford St., Burlington, Ma., 01803.

Intermission

WF7 (3:15)

MEASUREMENTS OF SELF-BROADENING OF OZONE ABSORPTION LINES

M. A. H. SMITH, C. P. RINSLAND, AND V. MALATHY DEVI

Self-broadened halfwidths at room temperature have been determined for 355 spectral lines of five different vibration-rotation bands of $^{16}\text{O}_3$ in the 4.8-17 μm region (ν_2 , ν_1 , $\nu_2+\nu_3$, $\nu_1+\nu_3$, and $2\nu_3$)¹. These results were obtained from absorption spectra recorded at 0.005 cm^{-1} resolution using the McMath Fourier transform spectrometer at the National Solar Observatory on Kitt Peak. The halfwidth values were obtained through a nonlinear least-squares spectral fitting procedure. The resulting self-broadening coefficients lie within the range of 0.08 to 0.12 $\text{cm}^{-1}\text{atm}^{-1}$ and are in good agreement with most of the previous measurements. No significant differences were observed between halfwidths of lines with the same J'' and K_a'' quantum numbers from band to band or from branch to branch within a band. The present study covers a sufficiently wide range of rotational quantum numbers (J'' up to 48, K_a'' up to 13) to permit a detailed examination of the variation of the ozone self-broadening coefficient with these quantum numbers.

¹M. A. H. Smith, C. P. Rinsland, and V. Malathy Devi, *J. Mol. Spectrosc.* **147**, in press (1991).

Address of Smith and Rinsland: NASA Langley Research Center, Atmospheric Sciences Division, Mail Stop 401A, Hampton, Virginia 23665-5225.

Address of V. Malathy Devi: Physics Department, The College of William and Mary, Williamsburg, Virginia 23185.

WF8 (3:27)

TEMPERATURE DEPENDENCE OF N_2 - BROADENING COEFFICIENTS IN THE ν_3 BAND OF OZONE

M. N. SPENCER AND C. CHACKERIAN, JR.

We report the first measurements of the temperature dependence of the nitrogen broadening coefficients of selected ozone rovibrational transitions. We recorded spectra of the ν_3 band at approximately 1000 cm^{-1} with a Bomem Fourier transform spectrometer at a resolution of 0.004 cm^{-1} and broadened by nitrogen at pressures ranging from 0 to 80 torr. The temperature was varied over the range of 180 K to 296 K in 20 K increments from one set of broadened spectra to the next. The pressure broadening coefficient, $\gamma(T)$, for a particular transition at a temperature, T , was obtained as the slope of a straight line plot of the collision broadened half-width vs. added nitrogen pressure. The dependence of the pressure broadening coefficient was assumed to be given by the power law,

$$\gamma(T)/\gamma(T_0) = (T/T_0)^n,$$

where T_0 is a reference temperature (296 K) and n is the temperature exponent. A plot of $\ln(\gamma(T))$ vs. $\ln(296 \text{ K}/T)$ therefore yields n . Values of n have been obtained for approximately 30 transitions in the ν_3 band and are close to the theoretically predicted average value of 0.76. We compare our experimentally determined temperature coefficients to those predicted by Quantum Fourier Transform theory¹.

¹R. Gamache, *J. Mol. Spectrosc.* **114**, 31 (1985).

Address of Spencer and Chackerian: NASA AMES Research Center, MS 245-4, Moffett Field, CA 94035-1000.

WF9 (3:44)**THE TEMPERATURE DEPENDENCE OF THE INFRARED ABSORPTION OF N_2O_5 IN THE REGION $300-400\text{ cm}^{-1}$** **B.P. WINNEWISSER, M. WINNEWISSER, F.C. DELUCIA, P. HELMINGER, G. SEIBERT AND G. PAWELKE**

It should be possible in the near future to observe the band of N_2O_5 in the atmospheric window between 300 and 400 cm^{-1} in addition to monitoring the band at 1254 cm^{-1} which has been observed in the stratosphere. In view of this possibility, we have measured the spectrum of N_2O_5 between 250 and 600 cm^{-1} over the temperature range from room temperature to -60°C at intervals of 10°C .

The measurements were made at resolutions of both 0.1 cm^{-1} and 0.01 cm^{-1} . Spectra of the two major impurities, NO_2 and HNO_3 , were run under the same conditions in order to compensate their contributions to the N_2O_5 spectra. Furthermore, a spectrum of N_2O_5 at a resolution of 0.002 cm^{-1} was run at -60°C . These data are being evaluated in an effort to obtain accurate intensity information for the N_2O_5 absorption in this spectral range.

Address of B.P. Winnewisser, M. Winnewisser and G. Seibert: Physikalisch-Chemisches Institut, Justus-Liebig-Universität, D-6300 Giessen, Germany.

Address of F.C. DeLucia: Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, Ohio 43210.

Address of P. Helminger: Department of Physics, The University of South Alabama, Mobile, Alabama 36688.

Address of G. Pawelke: Anorganische Chemie, FB 9, Universität-Gesamthochschule Wuppertal, D-5600 Wuppertal 1, Germany.

WF10 (4:01)**OXYGEN-INDUCED BROADENING AND LINE SHIFTS IN THE ν_3 REGION OF $^{12}\text{CH}_4$** **D. CHRIS BENNER, V. MALATHY DEVI, MARY ANN H. SMITH AND CURTIS P. RINSLAND**

A series of high-resolution room temperature spectra were recorded with dilute mixtures (1%) of methane in oxygen using the McMath Fourier transform spectrometer located at the National Solar Observatory on Kitt Peak. All spectra were obtained at 0.01-cm^{-1} resolution covering the $2650-3200\text{ cm}^{-1}$ spectral region; a 25-cm stainless steel absorption cell was used. Total sample pressures, which ranged between 100 and 400 Torr, were continuously monitored. Oxygen broadening and pressure-induced line shift coefficients for $^{12}\text{CH}_4$ lines were deduced by analyzing these spectra with a nonlinear least-squares method. Results were obtained for over 200 transitions in the ν_3 pentad. These results will be compared to similar work previously reported for air and nitrogen broadening of $^{12}\text{CH}_4$ in the same spectral region and for oxygen broadening of the same transitions in $^{13}\text{CH}_4$.

Address of Benner and Malathy Devi: Department of Physics, College of William and Mary, Williamsburg, VA 23185.

Address of Smith and Rinsland: Atmospheric Sciences Division, NASA Langley Research Center, Mail Stop 401A, Hampton, VA 23665-5225.

WF11 (4:18)

BROADENING AND SHIFTS OF CH₄ LINES IN THE ν_4 BAND AT LOW TEMPERATURES

M. A. H. SMITH, V. MALATHY DEVI, C. P. RINSLAND, AND D. C. BENNER

We have recorded a series of high-resolution absorption spectra of methane broadened by dry air and by N₂ at temperatures from -63°C to 2°C using the McMath Fourier transform spectrometer at the National Solar Observatory on Kitt Peak. The spectra cover a wavenumber range from approximately 500 cm⁻¹ to 1500 cm⁻¹ at a resolution of 0.01 cm⁻¹. These spectra have been analyzed to determine pressure broadening and line shift coefficients at low temperatures for over 150 lines in the ν_4 fundamental band of ¹²CH₄. These values, along with previous FTS measurements at room temperature¹, have been used to determine the temperature dependence of the air- and N₂-broadening and shift coefficients for these CH₄ lines. Recent TDL measurements of low-temperature N₂-broadening for a small group of lines² are in excellent agreement with our results. Since the present results cover a wide range of rotational quantum numbers (J'' up to 13), the variation of the halfwidths and shifts from line to line within the ν_4 band will be examined.

¹C. P. Rinsland, V. Malathy Devi, M. A. H. Smith, and D. C. Benner, *Appl. Opt.* **27**, 631-651 (1988).

²P. Varanasi and S. Chudamani, *J. Geophys. Res.* **94**, 13073-13078 (1989).

Address of Smith and Rinsland: Atmospheric Sciences Division, Mail Stop 401A, NASA Langley Research Center, Hampton, Virginia 23665-5225.

Address of Malathy Devi and Benner: Physics Department, College of William and Mary, Williamsburg, Virginia 23185.

WF12 (4:35)

DIODE LASER MEASUREMENTS OF CO₂ LINE INTENSITIES AT HIGH TEMPERATURE IN THE 4.3 μ m REGION

L. ROSENMANN, S. LANGLOIS, C. DELAYE, and J. TAINE

Diode laser measurements of low pressure CO₂ transmission spectra have been made up to 800 K in the 4.3 μ m region. Line intensities of several parallel hot bands with $\Delta v_3=1$ of ¹²C¹⁶O₂ have been obtained. The data were analyzed to derive vibrational band intensities. Our results are consistent with previous measurements performed at room temperature by Fourier transform spectroscopy. The results obtained for bands which, to our knowledge, have not been analyzed previously are compared with available theoretical predictions.

Address of Rosenmann, Langlois, and Taine : Laboratoire E.M.2.C du CNRS (UPR 288) et de l'ECP, Ecole Centrale Paris, Grande Voie des Vignes, 92295 Châtenay-Malabry Cedex, France.

Address of Delaye : Applied Physics Laboratory, The Johns Hopkins University, Laurel, Maryland 20723.

WF13 (4:47)

PRESSURE BROADENING MEASUREMENTS OF CH₄ AT 77°K BY H₂ AND He

Daniele Romanini and Kevin K. Lehmann

CH₄, broadened by H₂ and He, and at temperatures between 50-150 K, is the dominate absorber of the atmospheres of the outer planets. We are measuring the pressure broadening coefficients of individual ro-vibrational lines in the ν_3 fundamental band near 3.3 μm in a low temperature cell. In particular, we plan to measure the difference in broadening between ortho and para H₂.

Address of Romanini and Lehmann: Department of Chemistry, Princeton University, Princeton NJ 08544

WF14 (4:59)

FIRST OBSERVATION OF LINES CORRESPONDING TO THE $(03^1_0, 11^1_0)_{II}$ TO 00^0_1 VIBRATIONAL TRANSITION IN NITROUS OXIDE.

J. M. SIROTA, D. C. REUTER, and M. J. MUMMA

Measurements of strength, line position, and width were performed for rotational lines corresponding to the $(03^1_0, 11^1_0)_{II}$ to 00^0_1 vibrational transition in N₂O. These measurements constitute the first recording of such transitions in this species.

A tunable diode laser operating in the 21 μm spectral region was used as source. A White type cell with a path length of up to 100 meters contained the gas sample. A blocked impurity band (BIB) silicon detector refrigerated with liquid ⁴He was used as a detecting element.

Combination of fast sweep averaging and second derivative detection were applied to observe these low strength transitions. However, line strengths were determined by direct absorption measurements, which yielded absolute intensities.

Characteristics of the measured spectra obtained at several temperatures, as well as details of the technique, will be presented.

Address of authors: NASA Goddard Space Flight Center, Laboratory for Extraterrestrial Physics, Code 693, Greenbelt, Md, 20770

J. M. Sirota holds a National Research Council - NASA Research Associateship.

WG1 (1:30)

INSTRUMENTAL ADVANCES IN THE MEASUREMENT OF RAMAN OPTICAL ACTIVITY

D. CHE, G.-S. YU, T.B. FREEDMAN AND L.A. NAFIE

We have constructed a new Raman optical activity (ROA) spectrometer at Syracuse University that is equipped with a charge coupled device (CCD) detector, and zeroth-order quarter wave plates held in computer-controlled, motorized rotation mounts. Precise polarization modulation can be carried out for both the incident and scattered beams, either separately as in incident (ICP) and scattered (SCP) circular polarization modulation ROA, or synchronously in-phase (DCP_I) or out-of-phase dual circular polarization (DCP_{II}) ROA. We have carried out a variety of CP ROA measurements using both right-angle and backward scattering geometry. To date, we find that the depolarized Raman and ROA setup associated with backscattering DCP_I measurements is the optimum ROA configuration for the instrument that we have constructed. Examples of ROA spectra measured with this instrument will be presented which include backscattering DCP_I spectra of amino acids, sugars and peptides measured in either H₂O or D₂O. Comparisons will also be presented for various forms of CP ROA together with a comparison of the theoretical expressions associated with these forms.

Address of Che, Yu, Freedman and Nafie: Department of Chemistry, Syracuse University, Syracuse, New York 13244-4100.

WG2 (1:47)

VIBRATIONAL CIRCULAR DICHROISM AND RAMAN OPTICAL ACTIVITY IN EPHEDRINE MOLECULES

N. RAGUNATHAN, T. B. FREEDMAN, D. CHE, AND L. A. NAFIE

The vibrational circular dichroism (VCD) spectra in the OH-, NH- and CH-stretching regions, and the dual circular polarization (DCP_I) Raman optical activity (ROA) spectra in the 800-1700 cm⁻¹ region of (1*S*,2*R*)-ephedrine, (1*S*,2*R*)-norephedrine, (1*S*,2*S*)-pseudoephedrine, and (1*S*,2*S*)-norpseudoephedrine will be presented. The hydrogen stretching absorption spectra of the free base molecules in dilute C₂Cl₄ solution reflect differences in intramolecular hydrogen bonding among these amino alcohol drug molecules. The corresponding VCD features, which uniquely characterize each stereoisomer, will be correlated with the rotameric populations deduced from NMR studies. The Raman spectra, obtained for aqueous solutions of the hydrochloride salts, are nearly identical for the four ephedrines. In contrast, the ROA spectra are quite different. Several ROA features can be identified that serve as configurational markers.

Address of Ragunathan, Freedman, Che and Nafie: Department of Chemistry, Syracuse University, Syracuse, New York 13244-4100.

WG3 (2:04)

METHINE STRETCHING VCD IN HYDROXY ACIDS AND RELATED MOLECULES

D. M. GIGANTE, J. E. EVANS, T. B. FREEDMAN AND L. A. NAFIE

The methine stretching VCD spectra of a number of hydroxy acids and substituted hydroxy acids have been investigated. Deuterium substitution was used to remove overlapping absorption features when possible. For L-lactide, (*S*)-methyl-d₃ lactate, (*S*)-methyl-d₃ mandelate, di(methyl-d₃) L-tartrate, methyl-d₃ (2*S*)-methoxy-d₃-propionate, and (*S*)-O-acetylmandelic acid in nonaqueous solution, anisotropy ratios equal to $\sim 2.5 \times 10^{-4}$ were measured. Salts of hydroxy acids in aqueous solution exhibited similar large anisotropy ratios. In dimethyl-d₆-2,3-O-benzylidene-C-d₁-L-tartrate and (*S*)-methyl 2-chloropropionate, the methine stretching VCD intensity is quite small. The factors leading to a large methine VCD anisotropy ratio will be assessed.

Address of Gigante, Evans, Freedman and Nafie: Department of Chemistry, Syracuse University, Syracuse, New York 13244-4100.

WG4 (2:21)**VIBRATIONAL CIRCULAR DICHROISM OF (S,S)-OXIRANE-2,3-²H₂ AND (S,S)-CYCLOPROPANE-1,2-²H₂ IN THE GAS PHASE AND SOLUTION****T. B. FREEDMAN, N. RAGUNATHAN AND L. A. NAFIE**

Vibrational circular dichroism (VCD) spectra of two simple chiral three-membered ring molecules, (S,S)-oxirane-2,3-²H₂ and (S,S)-cyclopropane-1,2-²H₂ have been obtained for samples in the gas phase and in C₂Cl₄ and CS₂ solution. Due to electric dipole moment contributions from oxirane ring stretches, the A-symmetry modes are more intense than the B-symmetry modes in the mid-infrared region of (S,S)-oxirane-2,3-²H₂, whereas the mid-infrared B-symmetry are more intense in (S,S)-cyclopropane-1,2-²H₂. The signs and relative intensities of the VCD bands in both molecules can be understood in terms of chiral perturbation, due to the deuterium substitution, of the parent achiral oxirane or cyclopropane vibrations. This perturbation mixes modes of the parent molecule that involve linear charge oscillation along an axis with modes that involve angular charge oscillation about that same axis. Comparisons will be made of the observed rotational strengths with recent published VCD intensity calculations using various theoretical approaches.

Address of Freedman, Ragunathan and Nafie: Department of Chemistry, Syracuse University, Syracuse, New York 13244-4100.

WG5 (2:38)**VIBRATIONAL CIRCULAR DICHROISM STUDY OF [2S,3S]-DIDEUTERIOBUTYRO-LACTONE. COMPARISON OF EXPERIMENTAL AND CALCULATED SPECTRA.****PETR MALON, LORETTA J. MICKLEY, KATHLEEN SLUIJS, TIMOTHY A. KEIDERLING, JACK UANG, SID KAMATH, AND JAMES S. CHICKOS**

The title compound has been newly prepared, characterized and its infrared absorption and vibrational circular dichroism (VCD) spectra will be presented. The absorption intensities and VCD signs and magnitudes were calculated using the *a priori* theory of Stephens. The lowest energy conformation, as determined by *ab initio* energy minimization calculations, is a slightly distorted envelope form, thus deuteration gives rise to an axially and an equatorially substituted form for each isomer. An *ab initio* force field was determined at the 6-31G** basis set level for this conformer, and normal coordinates were determined for each substituent form. Good qualitative agreement was found between the experimental and theoretical dipole strengths and rotational strengths, also calculated at the 6-31G** level, when the average of the theoretical values for the two substituent forms was used. Calculations were also made for the planar conformation which corresponds to a higher energy minimum on the potential surface. These results will be compared to those with ones with a more optimized force field and one with more approximate calculations using partial charge methods.

Address of Malon, Mickley, Sluis and Keiderling: Department of Chemistry, University of Illinois at Chicago Box 4348, Chicago, IL 60680

Address of Uang, Kamath and Chickos: Department of Chemistry, University of Missouri St. Louis 8001 Natural Bridge Road, St. Louis, MO 63121

WG6 (2:55)**VIBRATIONAL CIRCULAR DICHROISM STUDY OF [3R,4R]-DIDEUTERIOCYCLOBUTANE-1,2-DIONE. COMPARISON OF EXPERIMENT AND CALCULATIONS.**PETR MALON, KATHLEEN SLUIS, TIMOTHY A. KEIDERLING, J. -Y. UANG AND JAMES S. CHICKOS

The preparation, infrared absorption and vibrational circular dichroism (VCD) spectra of the title compound will be presented. The absorption intensities and VCD signs and magnitudes were calculated using an *ab initio* force field and the *a priori* theory of Stephens, both carried out with a 6-31G** basis set at the SCF level. Excellent agreement was found between theory and experiment for the single-signed VCD seen in the C-H (+) and C-D (-) stretching regions. As predicted, no VCD was detectable in the C=O stretching region. The mid-ir VCD pattern from 1300 to 900 cm^{-1} consisting of two large negative bands and several weak positive bands, was well-represented by the calculations. The single conformation of relatively high symmetry appears to have led to a relatively simple vibrational spectrum which is particularly susceptible to these analyses. Difficulties with isotopic and chemical impurity interference are shown to be less in VCD. Calculations on related four member ring molecules will also be presented as time permits.

Address of Malon, Sluis and Keiderling: Department of Chemistry, University of Illinois at Chicago
Box 4348, Chicago, IL 60680

Address of Uang and Chickos: Department of Chemistry, University of Missouri St. Louis
8001 Natural Bridge Road, St. Louis, MO 63121

Intermission**WG7 (3:25)****EXPERIMENTAL AND AB INITIO THEORETICAL VIBRATIONAL CIRCULAR DICHROISM OF SUBSTITUTED OXIRANES**

P. L. POLAVARAPU, S. T. PICKARD, H. E. SMITH AND T. M. BLACK

Vibrational circular dichroism (VCD) spectra in the 1600-700 cm^{-1} region will be reported for trans-2,3-dimethyloxirane, trans-2,3-dimethyloxirane-2,3- d_2 and trans-2,3-dimethyloxirane-2- d_1 . These compounds were synthesized using a novel synthetic scheme developed by two of us (STP and HES). *Ab initio* localized molecular orbital (LMO) calculations have been carried out with 6-31G basis set. A quantitative comparison of the experimental and theoretical results will be presented.

Address of all authors: Department of Chemistry, Vanderbilt University, Nashville, TN 37235.

WG8 (3:42)**VIBRATIONAL CIRCULAR DICHROISM OF METHYL AND ETHYL LACTATES**

P. L. POLAVARAPU AND P. K. BOSE

Vibrational circular dichroism (VCD) spectra in the 1600-700 cm^{-1} region will be reported for the title compounds. The spectra were obtained for CCl_4 and CS_2 solutions. *Ab initio* localized molecular orbital (LMO) predictions of VCD for methyl lactate, obtained with the 6-31G* basis set, will also be presented. There is a remarkable agreement between the observed and predicted VCD spectra.

Address of Polavarapu Department of Chemistry, Vanderbilt University, Nashville, TN 37235.

Address of Bose: Department of Chemistry, Government B.M. College, Barisal, Bangladesh.

WG9 (3:54)

NEAR INFRARED CIRCULAR DICHROISM SPECTRA OF (3R)-METHYL CYCLOHEXANONE AND (3R)-METHYL CYCLOPENTANONE

S. ABBATE, G. LONGHI, L. LESPADE, D. CAVAGNAT, C. BERTUCCI, P. SALVADORI

The circular dichroism spectra of (3R)-Methyl cyclohexanone and (3R)-Methyl cyclopentanone have been recorded in the range 2000-800 nm, covering the vibrational overtone for $\Delta v=2, 3, 4$.

By comparing with the CD data for the same molecules at $\Delta v=1$ (1) and by considering the Birge-Sponer plots, a first assignment of the observed CD features will be proposed.

Due comparison will be made with the CD data that had been previously collected for some cyclic monoterpenes in the near infrared range (2). In the latter case higher rotational strengths had been measured.

¹L.A. Nafie, T.A. Keiderling, P.J. Stephens, J. Am. Chem. Soc., **98**, 2715 (1976)

²S. Abbate, G. Longhi, L. Ricard, C. Bertucci, C. Rosini, P. Salvadori, A. Moscowitz, J. Am. Chem. Soc., **111**, 836 (1989)

Address of Abbate and Longhi: Dipartimento di Chimica Fisica, Università di Palermo, via Archirafi 26, 90123 Palermo, Italy.

Address of Lespade and Cavnagat: Laboratoire de Spectroscopie Moléculaire et Cristalline, Université de Bordeaux I, Crs. de la Libération 351, 33405 Talence, France.

Address of Bertucci and Salvadori: Dipartimento di Chimica, Università di Pisa, via Risorgimento 35, 56100 Pisa, Italy.

WG10 (4:11)

BAND SHAPE OF THE CH₂ STRETCHING BANDS - SOLID POLYETHYLENE.

M. Grandbois, M. Trudel, and C. CHAPADOS

The infrared spectra of large molecules of biological interest such as proteins and lipids, show large structureless bands. To separate the components in the massive absorptions, it is necessary to know the band shapes and bandwidths of the functional groups involved in the absorption. We present here the case of the CH₂ stretching bands.

We used solid polyethylene obtained from an o-xylene solution as a model system for the CH₂ groups. The spectra at several thickness were obtained. Four bands were visually observed in the 2900 cm⁻¹ region. After Fourier deconvolution and band fitting, eight bands were retrieved: four for the CH stretch bands and four for the combination bands. The bandwidths are 13.3 and 6.9 cm⁻¹ for the anti- and symmetric CH₂ stretch band, respectively. The band shape ratio (Cauchy index over the sum of Cauchy and Gauss indices) is near 0.71 for the two cases. The method used to retrieve these values as well as the assignment of the bands will be presented.

Address of Grandbois, Trudel, and Chapados: Département de chimie-biologie, Université du Québec à Trois-Rivières, C.P. 500, Trois-Rivières, Qc, Canada, G9A 5H7

WG11 (4:28)

VIBRATIONAL CIRCULAR DICHROISM MEASUREMENTS IN THE FAR INFRARED REGION: STATUS REPORT P. L. POLAVARAPU

For vibrational circular dichroism measurements in the far infrared region (600-10 cm^{-1}), a interferometer with interchangeable polarization and amplitude divisions was developed. Preliminary measurements with the combination of CdSe wave plate and wire grid polarizer serving as 'sample' were carried out. These measurements, carried out with a room temperature detector as well as with a liquid helium cooled bolometer, indicated the correct behavior of the interferometer. Limited measurements were also done for real samples such as α -pinene. These results, current status and future developments will be summarized.

Address of P. L. Polavarapu: Department of Chemistry, Vanderbilt University, Nashville, TN 37235.

WG12 (4:40)

Theoretical Prediction of the Magnetic Circular Dichroism Spectrum in Cl_2 : The

$1^1\Pi_u \leftarrow X(^1\Sigma_g^+)$ Electronic Transition.

George F. Adams and Cary F. Chabalowski, US Army Ballistic Research Laboratory, SLCBR-IB-I, Aberdeen Proving Ground, MD 21006-5066

A newly implemented method based on first-order perturbation theory will be used to calculate the electronic magnetic circular dichroism (MCD) spectrum in Cl_2 . Specifically, the $1^1\Pi_u \leftarrow X(^1\Sigma_g^+)$ transition will be calculated via ab initio techniques including state-averaged CASSCF plus CI. Brith et al.¹ have predicted that the MCD intensity for this transition arises from a combination of both the d -term and g -term as defined by Stephens². The experimental work was supported by a crude theoretical treatment. It is the purpose of this study to investigate the origin of the intensity for the MCD signal of the

$1^1\Pi_u \leftarrow X(^1\Sigma_g^+)$, and determine the relative contributions of the d - and g -terms.

1. M. Brith, M.D. Rowe, O. Schnepp, and P.J. Stephens, Chem. Phys. **9**, 57 (1975).

2. P.J. Stephens, Adv. Chem. Phys. **35**, 197 (1976).

Address of Chabalowski and Adams: Ballistic Research Lab, SLCBR-IB-I, Aberdeen Proving Ground, MD 21006-5066.

WG13 (4:57)

PHOTOCHEMISTRY OF ACETONE ON NaCl FILMS: AN IR ANALYSIS HUGH H. RICHARDSON

The photochemical products of acetone adsorbed on a NaCl film are determined by Fourier Transform Infrared Spectroscopy. Monolayer acetone on an annealed NaCl film is first characterized using FTIR spectroscopy and then radiated with UV light from a broad band Xe lamp (75 Watts). Difference spectra (before and after radiation) reveal the photochemical products of which CO and CH_4 are the major products. Excitation of gas phase acetone with 193 nm light yields only methyl radicals and CO with a quantum yield near unity. The methane produced after excitation is believed to be from surface aligned photoreaction of methyl radical and neighbor acetone molecules.

Address of Richardson: Department of Chemistry, Ohio University, Athens, OH 45701.

WH1 (1:30)

Stark Effects in the Far-Infrared Vibration-Rotation-Tunnelling Spectrum of Propane-Water

David W. Steyert, Matthew J. Elrod, R. D. Suenram, and Richard J. Saykally

One of the Berkeley Tunable Far-Infrared Spectrometers has recently been modified for the observation of Stark effects, to help assign spectra observed in an argon-propane-water expansion. In the region from 16.6 to 24.8 cm^{-1} , 400 zero-field lines have been observed, some of which show Stark effects, and a few show well-resolved Stark splittings. The structure and dynamics of propane-water will be discussed in light of these results.

Address of Steyert, Elrod, & Saykally: Department of Chemistry,
University of California, Berkeley, CA 94720 USA
Address of Suenram: Molecular Physics Division, National Institute of Standards
and Technology, Gaithersburg, MD 20899 USA

WH2 (1:47)

TUNABLE FAR INFRARED LASER SPECTROSCOPY OF Ar_2HCl M.J. ELROD, D.W. STEYERT, AND R.J. SAYKALLY

This work reports the observation of far infrared intermolecular vibration-rotation bands assigned to the van der Waals trimer Ar_2HCl .

A recently constructed tunable far infrared laser spectrometer was used to measure van der Waals stretching and bending transitions in the 35-45 cm^{-1} region. Both chlorine isotopes were observed and nuclear quadrupole hyperfine splittings were resolved for each vibrational transition.

The observed frequencies were fit to a Watson S-reduced Hamiltonian to determine band origins and rotational constants for each state. In addition, the nuclear quadrupole hyperfine splittings were fit to determine the average angular orientation of the HCl monomer within the cluster.

One of the observed bands ($\nu_0 = 39.5 \text{ cm}^{-1}$) appears to be the Σ bending transition¹, as this state shows considerable spectroscopic similarity to the Σ bend of ArHCl . A second band ($\nu_0 = 37.2 \text{ cm}^{-1}$) evidences extensive vibrational state mixing, as the rotational constants indicate the existence of Ar-Ar stretching. This information reveals that the reversed adiabatic dynamical approximation made by Hutson, *et al.* in their theoretical study of three-body effects in Ar_2HCl^2 is inappropriate for the dynamics presently observed in the this system. Our results indicate the sensitivity of spectroscopic measurements to the details of the total intermolecular potential energy surface.

¹M.J. Elrod, D.W. Steyert, and R.J. Saykally, *J. Chem. Phys.* 94, 58 (1991).

²J.M. Hutson, J.A. Beswick, and N. Halberstadt, *J. Chem. Phys.* 90, 1337 (1989).

Address: Department of Chemistry, University of California, Berkeley 94720.

WH3 (2:04)

AlH EINSTEIN EMISSION COEFFICIENTS OF THE $A^1\Pi - X^1\Sigma^+$ TRANSITION

Jane K. Rice, Louise Pasternack and H.H. Nelson

The $A^1\Pi$ state of AlH has two bound vibrational levels, $v = 0$ and 1, a small barrier to dissociation and a dissociation energy, D_0 , of 0.24 ± 0.01 eV ($X^1\Sigma^+$ state: $D_0 = 3.1 \pm 0.01$ eV).¹ The diagonal transitions between these vibrational levels and the ground state are observed by the LIF technique. Triethylaluminum (TEAL) is photodissociated at 248 nm to produce ground state AlH which is subsequently excited by a second laser at either 425 nm (0,0 R3) or 436 nm (1,1 Q2).

Relative strengths of the various bands ($\Delta v = 0, \pm 1$) were assessed by collecting dispersed emission spectra. Ratios of Einstein emission coefficients and vibrational transition probabilities indicate that transitions occur mainly in the diagonal elements with the off diagonal elements two orders of magnitude lower. Comparison with theoretical predictions of the AlH and the analogous BH potential energy surfaces are made.

¹ P. Baltayan and O. Nedelec, *J. Chem. Phys.*, 70, 2399 (1979).

Address of Rice, Pasternack and Nelson: Chemistry Division, Naval Research Laboratory, Washington, DC 20375-5000

WH4 (2:21)

THE STRUCTURE AND PHOTOPHYSICS OF BENZENE-(H₂O)₁ AND BENZENE-(H₂O)₂ COMPLEXES

Albert J. Gotch, Aaron W. Garrett, Daniel L. Severance, and Timothy S. Zwier

The intermolecular potential between aromatic and water moieties is of considerable interest because of its important role in determining properties such as immiscibility of the bulk liquids and the conformational preferences of biomolecules in aqueous solution. In order to deepen our understanding of such systems, we have carried out detailed R2PI studies on benzene-H₂O and benzene-(H₂O)₂ clusters formed in a supersonic expansion. Spectroscopic evidence is presented indicating in the 1:1 complex the H₂O molecule is on the six-fold axis in a π hydrogen-bonding configuration with free internal rotation about this axis. Rotational band contours have been obtained of the 1:1 complexes of benzene with H₂O, HDO, and D₂O at 0.08 cm⁻¹ resolution. The class structure and character table of a new molecular symmetry group, G₂₄, associated with these complexes has been constructed for the analysis.

For the 1:2 complex the rotational band contour indicates the two water molecules bind to benzene on the same side of the benzene ring, with a H₂O-H₂O separation close to that in the water dimer.

The van der Waal's structure of the 1:1 and 1:2 complexes and their isotopomers has been analyzed and tentative assignments are presented.

Address of authors: Department of Chemistry, Purdue University, West Lafayette, IN 47907

WH5 (2:33)

MULTIPHOTON IONIZATION STUDIES OF CLUSTERS OF IMMISCIBLE LIQUIDS. Aaron W. Garrett, Albert J. Gotch, and Timothy S. Zwier

Mixed clusters of type (C₆H₆)₁-(H₂O)_n where $n=3-8$ (i.e., 1:n) have been studied using one-color resonance-enhanced two-photon ionization with time-of-flight mass spectrometric detection. The S₀-S₁ spectra obtained by monitoring the 1:2, 1:3, and 1:4 masses are remarkably similar in appearance. Several pieces of spectroscopic evidence will be presented that these clusters are forming tight, hydrogen-bonded networks of water molecules building off one face of the benzene ring, reflecting the immiscibility of the bulk liquids.

Absorption features of higher clusters first shift further blue, and then rapidly to the red, with extensive van der Waals' structure simultaneously appearing in the spectra. This general development is suggestive of the hydrogen bonded water network beginning to fold around the benzene molecule.

Metastable ion studies using a reflectron TOFMS were also carried out on these clusters. For a given parent cluster, 1:n, metastable ion peaks were observed corresponding to loss of 1 to n water molecules.

Address of authors: Department of Chemistry, Purdue University, West Lafayette, IN 47907

WH6 (2:45)

THE SPECTROSCOPY AND PHOTOPHYSICS OF 2-,4- AND 5-METHYLPYRIMIDINE.

Ralph E. Bandy, Aaron W. Garrett, John Nash, and Timothy S. Zwier

A spectroscopic study of the effect of the position of methyl substitution on the photophysics of methylpyrimidines has been carried out. Of particular interest is the effect the substitution position has on the barrier to internal rotation.

Laser-induced fluorescence excitation was used to probe the S_1 states of jet-cooled 4-, 5- and 2-methylpyrimidine. The S_0 state was probed using dispersed fluorescence. In the case of 5-m-p, assignments could readily be made via comparison with the spectroscopy of unsubstituted pyrimidine. Furthermore, a nearly free rotor is seen in both S_0 and S_1 . With the reduction in symmetry in 4-m-p, we see a 100 cm^{-1} barrier in S_0 with a 7-fold increase upon going to S_1 . In addition, the spectroscopic influence of the methyl group is more prevalent in 4-m-p than in 5-m-p. It appears at the present time that 2-m-p exhibits much the same spectroscopy as seen in 5-m-p, particularly with respect to internal rotation.

Address of authors: Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

WH7 (3:10)

THE MAGNETIC ROTATION SPECTRUM OF $^{79}\text{Br}_2$ ($A^3\Pi_{1u} - X^1\Sigma_g^+$)

A. CHANDA, F.W. DALBY, L. OZIER and J. SANDERS

We have investigated the resonant Magnetic Rotation Spectrum of the weak $A^3\Pi_{1u} - X^1\Sigma_g^+$ electronic band of isotopically pure $^{79}\text{Br}_2$. With absorption techniques¹, overlap with the very strong $B^3\Pi_{0u} - X^1\Sigma_g^+$ electronic band at all wavelengths makes the weak A-X system particularly difficult to study. On the other hand, the magnetic rotation technique has strongly suppressed the overlapping B-X electronic band, and the resulting Magnetic Rotation Spectrum of the weak A-X band had a signal-to-noise ratio of at least 350 on a typical line. This technique is extremely sensitive to low J lines which are otherwise very difficult to observe at room temperature.

¹ J.A. Coxon, J. Mol. Spec., **41**, 548 (1972).

This work was carried out at: Department of Physics, University of British Columbia, Vancouver, B.C., Canada V6T 1Z1.

Permanent address of Sanders: Physics Department, Univ. of Oxford, Oxford, England.

WH8 (3:27)

A SPECTRAL AND X_{e} STUDY OF THE $\text{Cr:Mg}_2\text{SiO}_4$ CRYSTAL

B.C. YANG, Y. Q. LIN, P. LIN, AND I. S. CHENG

$\text{Cr:Mg}_2\text{SiO}_4$ is a new, promising laser crystal with a wavelength range from $1.1\mu\text{m}$ to $1.3\mu\text{m}$, but the mechanism of its laser center still remains to be explored.

A preliminary study of the electronic structure of the center, in both experiment and theory, has been carried out with systematic data obtained.

Experimentally, the normal and polarized transmission spectra, and the LIF spectra of the crystal at room temperature and liquid nitrogen temperature were obtained and analyzed. Both the absorption and fluorescence spectra are the most systematic up to now. It was proved that there should be other types of optical centers besides Cr^{3+} in the crystal which is of importance to the laser action.

MS- X_{e} calculations were made in the theoretical study. The electronic structure data and energy diagrams of several optical center models which may exist in the crystal were obtained. Comparing the theoretical results with the experimental spectra, the author confirms that the complex $(\text{CrO}_4)^{4-}$ is the best model of the new optical center which is responsible for the laser emission though $(\text{CrO}_4)^{3-}$ might also be a reasonable model.

Address: Physics Department, East China Normal University, Shanghai 200062, P.R.China.

WH9 (3:39)

OBSERVATION OF THE $j=2$, $|k|=1$ LEVELS OF Ar-NH_3 BY FAR INFRARED DIFFERENCE FREQUENCY - SIDEBAND SPECTROSCOPY

S.W. Reeve, M.A. Dvorak, A. Grushow, W. Burns, and K.R. Leopold

The states of the weakly bound complex Ar-NH_3 correlating to $j=2$, $|k|=1$ NH_3 have been observed using a CO_2 laser difference frequency - microwave sideband spectrometer. Over 150 transitions have been recorded in the vicinity of 48 cm^{-1} . Definitive assignment of several subbands originating in both Σ and π states of the $j=1$, $|k|=1$ complex, and terminating in the upper π component of the $j=2$, $|k|=1$ complex have been made using combination differences. Assignment of additional subbands are in progress. The spectra are discussed in relation to previous work on this system.

Address of Reeve, Dvorak, Grushow, Burns, and Leopold: Department of Chemistry, University of Minnesota, Minneapolis, MN 55455

WH10 (3:56)

THE $\text{C}^3\Pi$ STATE OF THE SO RADICAL C. CLERBAUX AND R. COLIN

The $\text{B}^3\Sigma^- - \text{X}^3\Sigma^-$ emission spectrum of the SO radical has been reinvestigated at high resolution from a microwave discharge in SO_2 using a Bruker FTS 120HR spectrograph.

Since 1932¹, the $\text{B}^3\Sigma^-$ state has been known to undergo predissociation and to present complex rotational perturbations on the $v=1, 2$ and 3 vibrational levels, but no satisfactory analysis² of these features, caused by a $\text{C}^3\Pi$ state, has been performed.

A new attempt which investigated both S^{16}O and S^{18}O isotopomers has led to new information concerning the $\text{C}^3\Pi$ state and will be presented.

¹ E. Martin, Phys. Rev. **41**, 167 (1932)

² D. Abadie, Ann. Phys. **5**, 227 (1970)

Address of authors : Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles, 50 av. F.D. Roosevelt, 1050 Brussels, Belgium.

FA4(4:08) and FA5(4:25) will be presented here at the request of the author who must return to Japan on Friday.

RA1 (8:30)**H₂S AND NH₃: VIBRATION - ROTATIONAL INTERACTIONS**

Invited Paper. 30 min.

S. URBAN, Czechoslovakia Academy of Science, Prague, Czechoslovakia.**RA2 (9:03)****GAS PHASE MAGNETIC VIBRATIONAL CIRCULAR DICHROISM. A POSSIBLE WAY TO DETERMINE THE ROTATIONAL g-FACTOR OF THE MOLECULAR ZEEMAN EFFECT**BAOLIANG WANG AND TIMOTHY A. KEIDERLING

We have focused on gas phase, rotationally resolved magnetic vibrational circular dichroism (MVCD) recently. The MVCD measurements of some small molecules were made at 0.5 cm⁻¹ resolution using an FTIR spectrometer with a superconductive magnet operated at 8T. These show that the MVCD A-terms caused by the first order molecular Zeeman effect provide information with regard to the sign and magnitude of the rotational g-factor for the excited vibrational state being observed in the infrared transition. The negative A-terms of some T_d group molecules, CH₄ and CD₄, and of some C_{3v} group molecules, NH₃ and ND₃, give evidence of a positive g_J. By use of moment analysis we can calculate A₁/D₀ which can be related to g_J by $A_1/D_0 = 2(\mu_N/\mu_B)g_J$. The g_J values we obtained for ν₄ of CH₄ and for ν₂ of NH₃ are +0.44 and +0.9 respectively. The difference from the ground vibrational state g_J values, which were measured by molecular beam magnetic resonance technique may be due to the limitations of our low resolution instrument or to the vibrational contribution.

Address: Department of Chemistry, University of Illinois at Chicago, Box 4348, Chicago, IL 60680, USA.

RA3 (9:20)**INFRARED SPECTRA OF CO-H₂ and CO-D₂ COMPLEXES IN THE 4.7 μM REGION**A.R.W. MCKELLAR

Well resolved spectra of CO-hydrogen complexes have been obtained in the region of the CO fundamental band using a long path absorption cell and a Bomem DA3.002 spectrometer. Typical experimental conditions are: path = 84 m; temperature = 50 K; CO pressure = 0.2 Torr; and hydrogen pressure = 5 Torr. Spectral lines of the complexes appear as relatively weak fine structure between the strong, broad (saturated) lines of ¹²C¹⁸O and are accompanied by a few sharp lines from the other CO monomer isotopes. It can be safely assumed that hydrogen is almost freely rotating in the complex, and spectra have been recorded using para-H₂ (which is entirely in its J=0 rotational state at this temperature), normal H₂ (25% J=0, 75% J=1), and ortho-D₂ (100% J=0). As expected, the CO-H₂ spectrum is quite different for the para- and normal H₂ samples. The CO constituent of the complex is, however, not free to rotate, and in terms of its motion the complex lies between the free internal rotation and semirigid molecule limits.

By analogy with spectra of CO-Ar and CO-Ne recorded under similar conditions, it is possible to assign some of the lines in the CO-H₂ and CO-D₂ spectra for the J=0 hydrogens; all of these species behave to some extent as T-shaped triatomics. However, the present challenge is to assign the spectra more completely, and it appears that some input from theoretical calculations using a realistic intermolecular potential will be necessary to accomplish this. Ultimately these results should help to define the potential much better than it is currently known, and they will also yield useful predictions for the as yet unobserved millimeterwave spectrum of CO-H₂.

Address: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.

RA4 (9:37)

FAR INFRARED SPECTRA OF HYDROGEN DIMERS: COMPARISON OF EXPERIMENT AND THEORY

A.R.W. MCKELLAR AND J. SCHAEFER

(H₂)₂ and (D₂)₂ have been studied in the 150 - 600 cm⁻¹ far infrared region using a Bomem Fourier transform spectrometer together with long absorption paths (~100 m) at very low temperature (20 K) and moderate pressures (20-50 torr). Close coupled calculations have been made for these systems using an intermolecular potential surface which is based on ab initio results, but empirically modified to better fit a variety of experimental data, and an ab initio dipole moment surface.

In this talk, the experimental and theoretical results are compared. For the S₀(0) transition in (H₂)₂, near 350 cm⁻¹, the comparison involves the entire band shape, including the free-free (collision-induced), bound-free, and bound-bound contributions. The agreement is generally very good except for the region from about 360-370 cm⁻¹ which is dominated by the broad $l = 3 \pm 0$ bound-free resonance. For the analogous S₀(0) transition in (D₂)₂, near 180 cm⁻¹, there are many more sharp well-resolved lines in the spectrum. The theoretical results for these discrete bound-bound lines are in good agreement with experiment, both in position and intensity. The remaining small deviations between theory and experiment should be useful for further refining the potential surface to include its dependence on the individual hydrogen bond lengths, which, of course, vary slightly with isotope, vibrational state, and rotational state.

Address of McKellar: Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.

Address of Schaefer: Max-Planck-Institut für Physik und Astrophysik, Institut für Astrophysik, D-8046 Garching, Germany.

RA5 (9:54)

VARIATIONAL SEPARATION OF ANGULAR AND RADIAL MOTIONS: THE GROUND VIBRATIONAL STATE OF AR-HCN

David Yaron and William Klemperer

The microwave spectrum of Ar-HCN, while superficially that of a linear molecule, exhibits a number of anomalies.^{1,2} The bending amplitude and the centrifugal distortion constants are 1) much larger than expected and 2) unusually sensitive to isotopic substitution. A pseudo-one dimensional model for the ground vibrational state will be discussed. Our model potential is of the form:

$$V(\theta, R) = V_\theta(\theta) + k(R - R_c(\theta))^2 \quad (1)$$

(where θ is the angle the HCN makes with the vector connecting the centers of mass of the two subunits, and R is the length of that vector.) The potential is arbitrary along the reaction path, $R_c(\theta)$, but is harmonic in R about this path. The following form for the wavefunction is assumed:

$$\Psi(\theta) = \psi(\theta) \left(\frac{2}{\pi\gamma(\theta)} \right)^{\frac{1}{4}} \exp \left(\frac{-(R - R_c(\theta))^2}{\gamma(\theta)} \right) \quad (2)$$

The functions, $\psi(\theta)$, $\gamma(\theta)$ and $R_c(\theta)$ are determined variationally. Notice that the maximum of the gaussian, $R_c(\theta)$, is not constrained to lie along the minimum of the potential $R_c(\theta)$. Unfortunately, only the lowest state of a given symmetry (Σ , Π , etc.) can be obtained. The method is checked against solutions of the full two-dimensional vibrational Hamiltonian.

We find that the ground state data can be quantitatively explained by a potential which allows sampling of the T-shaped, Ar-HCCH like, geometry. (The T-shaped geometry is not classically allowed but significant penetration into the region does occur). There is also a large coupling of angular and radial motions: $R_c(\theta)$ decreases from 4.62 Å to 3.76 Å as the molecule bends from the linear to the T-shaped geometry. This combination of tunneling and large angular-radial coupling gives rise to the unusual centrifugal distortion and isotope effects.

1) K.R. Leopold, G.T. Fraser, F.J. Lin, D.D. Nelson, and W. Klemperer, J. Chem. Phys. **81** (11), 4922 (1984).

2) T.D. Klots, C.E. Dykstra, and H.S. Gutowsky, J. Chem. Phys. **90** (1), 30 (1989).

Address of Yaron and Klemperer: Dept. of Chemistry, Harvard University, Cambridge, MA 02138.

RA6 (10:11)

MODELING THE HIGHLY EXCITED BENDING STATES, $v_2 = 26 \rightarrow 42$, OF $\tilde{X}, {}^1\Sigma^+ \text{HCP}$

David Yaron, Yit-Tsong Chen, Robert Silbey and Robert W. Field

Stimulated emission pumping (SEP) spectroscopy, using the bent $\tilde{A}, {}^1A''$ electronic state as an intermediate, allows access to highly excited bending states of HCP¹. To date, the vibrational states $[(0,26 \rightarrow 42, 0)$ and $(0,24-26,1)$; with v_2 even] have been observed. At this level of excitation, the classical turning points in the bend should be larger than 90°, and the hydrogen should be approaching the point where the bonding changes from predominantly C-H to predominantly P-H. At this point, the bending coordinate must change from an arc around the C to an arc around the P. It is surprising, therefore, that the spectra are relatively clean and the vibrational spacings do not deviate strongly from a harmonic pattern. There is, however, unusual behavior in the rotational constant and g_{32} (i.e., the energy difference between the $l=0$ and $l=2$ states). The rotational constant, which had been slowly decreasing with v_2 up to $v_2=34$, begins to increase rapidly for $v_2 > 34$, indicating a shortening of the CP bond as the molecule bends past 90°. Similarly, g_{32} , which changed very little between $v_2=0$ and 30 (from 5.0442(4)cm⁻¹ to 5.651(2)cm⁻¹), begins to increase rapidly above $v_2=34$ and by $v_2=40$ is 8.32cm⁻¹.

Although the SEP experiment is probing regions of very high energy, over 25000 cm⁻¹, the spectrum is relatively clean; essentially all of the energy is being deposited in the bending coordinate. This suggests that the bending is effectively a one dimensional motion. Since the C-P bond length decreases for $v_2 > 34$, the one dimensional motion must be occurring along a reaction path which includes changes in the bond lengths. The use of methods, such as the semi-rigid bender², which reduce the multi-dimensional problem to motion along a single reaction coordinate will be discussed.

1) Y. Chen, D.M. Watt, R. Field and K.K. Lehmann, J. Chem. Phys. **93**, 2149 (1990).

2) P.R. Bunker and B.M. Landsberg, J. Mol. Spectrosc. **67**, 374 (1977).

Address of Yaron, Chen, Silbey and Field: Dept. of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

Intermission

RA7 (10:35)

DETERMINATION SCHEMES.

M.VILLA, F.J.MELENDÉZ AND R.GIL

The model Hamiltonian proposed by Watson and Brown et al²

$$H = \sum h_i O_i + \sum h_i^s O_i^s$$

is widely used for fitting the rotational spectra of molecules with an unpaired electron and D_{2h} symmetry. The linear dependence among the molecular constants has been eliminated with a reduction scheme².

The model Hamiltonian and the number of molecular constants which participate in a reduction scheme can be divided in terms of order of magnitude. The value of zero (reduction scheme) is not the only one that can give a set of linearly independent molecular constants (determination scheme).

In order to have a good fit to the spectrum the order of magnitude must be preserved, which constrains the range of possible values assigned to each molecular constant involved in the determination scheme.

The fourth and eight order of magnitude constants behavior during a fitting have been studied according to the asymmetry parameter (K) of the molecule. It has been established a set of equations relating two possible sets of constants in terms of transformation parameters. The transformation parameters between two possible schemes of determination have been evaluated.

¹ J.K.G. Watson, J. Chem. Phys., **46**, 1935 (1967).

² J.M. Brown and T.J. Sears, J. Mol. Spectrosc., **75**, 111, (1979).

Address of Villa, Meléndez and Gil: Area de Química Cuántica, Universidad Autónoma Metropolitana Iztapalapa, Av. Michoacán y La Purísima, Iztapalapa, Apartado Postal 55-532, C.P. 09340, México D.F. Tels. 686-03-22, 686-16-11.

RA8 (10:52)

MOLECULAR-BEAM OPTOTHERMAL SPECTROSCOPY OF THE $9.6 \mu\text{m}$ ν_{14} BAND OF BENZENE

M.-L. JUNTILA, J.L. DOMENECH, G.T. FRASER AND A.S. PINE

The ν_{14} e_{1g} fundamental band of C_6H_6 has been recorded with sub-Doppler resolution under collisionless low-temperature molecular-beam conditions using bolometric detection of molecules excited by tunable microwave sidebands of a Lamb-dip-stabilized CO_2 laser. The sidebands cover about 40% of the spectrum between laser lines in which 117 transitions for $J, K \leq 11$ have been observed. The overall weighted standard deviation of ± 24 kHz yields improved ground and excited state rotational constants with nearly microwave accuracy. Our measured ground state rotational constant, $B_0 = 0.18977389(3) \text{ cm}^{-1}$, is compared with several disparate values reported previously.

Address: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

RA9 (11:09)

THE ν_{12} BAND OF BENZENE REVISITED

J.L. DOMENECH, M.-L. JUNTILA AND A.S. PINE

The highly accurate B_0 value for C_6H_6 found in a molecular-beam CO_2 -laser-microwave-sideband study of the 1038 cm^{-1} ν_{14} perpendicular band (above paper) is inconsistent with a previous Doppler-limited difference-frequency-laser spectrum of the 3048 cm^{-1} ν_{12} band [J. Pliva and A.S. Pine, J. Mol. Spectrosc. **93**, 209 (1982)]. Therefore we have recorded the molecular-beam optothermal spectrum of ν_{12} excited by a linear-scan-controlled color-center laser drift stabilized by reference to a dual-wavelength polarization-stabilized He/Ne laser. The low effective beam temperature (~ 8 K) completely eliminates spectral congestion, and the sub-Doppler instrumental linewidth (~ 15 MHz) permits resolution of essentially every transition. Revised assignments and new spectral constants will be reported.

Address: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

RA10 (11:26)

MOLECULAR-BEAM OPTOTHERMAL SPECTRUM OF THE OH STRETCHING BAND OF METHANOL.

I. KLEINER, G. T. FRASER, J. T. HOUGEN AND A. S. PINE.

The OH stretching fundamental band, ν_1 , of CH_3OH has been recorded with sub-Doppler resolution using a color-center laser molecular-beam optothermal spectrometer. The low effective rotational-vibrational temperature ($T_{\text{rot}} \sim 6$ K) of the molecular beam greatly reduces the spectral congestion from hot torsional vibrations and high rotational levels seen at room temperature, permitting an essentially complete assignment, a fit to a global hindered internal-rotor Hamiltonian, and identification of several perturbations and their likely perturbers. The rms deviation of the fit obtained when the perturbing levels were taken out is of the order of 0.001 cm^{-1} . The stronger local perturbations which affect the E species ($\sigma = \pm 1$), $K = -1$ and $K = -2$ levels appear to be $\Delta K = 0$ parallel-Coriolis or Fermi interactions with combinations of CH stretching modes plus three quanta of torsion. Further study of torsion-assisted couplings between OH stretching vibrations and the CH stretching vibrations are needed, however, to fully understand the perturbations in this spectrum. The present results suggest a torsional barrier of $439(13) \text{ cm}^{-1}$ in the excited state, compared to the ground state value of $\sim 373 \text{ cm}^{-1}$.

Address of Kleiner, Fraser, Hougen and Pine: Molecular Physics Division, National Institute for Standards and Technology, Gaithersburg, MD 20899, USA.

RA11 (11:43)

FTIR SPECTRA AND RO-VIBRATIONAL ANALYSIS OF OC10

J. ORTIGOSO, R. ESCRIBANO, J.B. BURKHOLDER, C.J. HOWARD and W.J. LAFFERTY

The spectra of all 3 fundamental bands and 2 overtone bands, $2\nu_1$ and $2\nu_3$, of OC10, have been obtained with a resolution of $0.004\text{--}0.006\text{ cm}^{-1}$, and the analysis of these spectra has now been completed. Last year at this meeting, we reported the experimental details of this work as well as a description of a computer program specifically designed to deal with the spectra of molecules where spin-rotation effects are present. Details of an analysis of the ν_1 band were also presented.

This year we discuss the analysis of the remaining fundamentals and the observed overtone bands (the $2\nu_2$ band is very weak and overlapped by the strong ν_1 fundamental). Ro-vibrational parameters for all excited states have been determined including centrifugal distortion spin-rotation constants. With all the accumulated information, including all the available microwave data, we have also carried out a ground state combination difference refitting which has yielded very precise parameters for the ground state.

The computer program has been extended to deal with the intensities of the absorption transitions which permits us to reproduce the observed intensity patterns of the split ro-vibrational lines. Details of this part of the program will be also presented.

Address of Ortigoso and Escribano: Instituto de Estructura de la Materia, Consejo Superior de Investigaciones Cientificas, Serrano 119, 28006 Madrid, Spain

Address of Burkholder and Howard: Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO 80303.

Address of Lafferty: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

RB1 (8:30)**IDENTIFICATION OF B AND C-TYPE CORIOLIS INTERACTIONS IN \tilde{A}^1A_u ACETYLENE-D₂ USING DOUBLE RESONANCE SPECTROSCOPY****J.K. Lundberg and R.W. Field**

The identification of B and C-type Coriolis interactions in the \tilde{A}^1A_u state is greatly facilitated by recording double resonance spectra to the vibrationless level of the previously assigned \tilde{C}^1A_g electronic state¹ of C₂D₂.

Analysis of the J and K rotational structure manifest in the double resonance spectra of the \tilde{C}^1 state allows the identification of B and C-type Coriolis perturbations in the \tilde{A} state. This analysis can provide direct evidence of the location of the dark A_g and B_g symmetry vibrational states involving ν_4 , ν_5 and ν_6 excitation in the still not fully characterized \tilde{A}^1A_u state of acetylene.

¹J.K. Lundberg, Y. Chen, J.P. Pique, and R.W. Field to be published

RB2 (8:47)**ELECTRONIC SPECTROSCOPY OF JET-COOLED ORGANOMETALLIC FREE RADICALS PREPARED BY A LASER VAPORIZATION/PHOTOLYSIS TECHNIQUE****Andrew M. Ellis, Eric S. J. Robles, and Terry A. Miller**

A simple laser vaporization/photolysis technique capable of preparing a wide variety of organometallic free radicals for spectroscopic studies is described. It makes use of an excimer laser which vaporizes a metal sample and simultaneously photolyzes an organic precursor passing over the surface of the metal. The metal atoms and organic fragments then react to yield the organometallic species. Subsequent expansion into vacuum leads to extensive cooling of the molecules. In principle, this approach could be used to prepare a wide variety of gas-phase compounds of any metal. We will illustrate its capabilities by presenting laser excitation spectra of several relatively simple organometallic radicals such as CaCH_3 , CdCH_3 , and CaC_3H_3 .

Address of authors: Laser Spectroscopy Facility, The Ohio State University,
120 W. 18th Avenue, Columbus, OH 43210

RB3 (9:04)**LASER EXCITATION SPECTROSCOPY OF ZINC AND CADMIUM CYCLOPENTADIENIDES****Eric S. J. Robles, Andrew M. Ellis, and Terry A. Miller**

Electronic spectra of zinc cyclopentadienide (ZnC_5H_5) and cadmium cyclopentadienide (CdC_5H_5) will be presented. Preparation of these radicals, neither of which has been observed previously in the gas phase, was achieved using a laser vaporization/photolysis technique. The $\tilde{A}-\tilde{X}$ and $\tilde{B}-\tilde{X}$ electronic transitions of both of these molecules have been recorded. Assignments of the symmetries of the low-lying electronic states of ZnC_5H_5 and CdC_5H_5 will be given and an analysis of the vibrational structure observed in their spectra will be discussed.

Address of authors: Laser Spectroscopy Facility, The Ohio State University,
120 W. 18th Avenue, Columbus, OH 43210

RB4 (9:16)**LASER EXCITATION SPECTROSCOPY OF THE MONOPYRROLIDE DERIVATIVES OF ZINC AND CADMIUM**Eric S. J. Robles, Andrew M. Ellis, and Terry A. Miller

Laser excitation spectra of the monopyrrolides $\text{ZnC}_4\text{H}_4\text{N}$ and $\text{CdC}_4\text{H}_4\text{N}$, cooled in a free jet expansion, will be presented. This study represents the first gas-phase spectroscopic observation of these organometallic radicals. Several electronic transitions of these molecules have been assigned from their excitation spectra. Furthermore, extensive vibrational structure, originating from both metal-ring and intra-ring vibrational modes, has been observed and will be discussed.

Address of authors: Laser Spectroscopy Facility, The Ohio State University,
120 W. 18th Avenue, Columbus, OH 43210

RB5 (9:28)**LASER EXCITATION SPECTROSCOPY OF THE MONOMETHYLCYCLOPENTADIENYL COMPLEXES OF CALCIUM, ZINC AND CADMIUM**Eric S. J. Robles, Andrew M. Ellis, and Terry A. Miller

Using a laser vaporization/photolysis technique, we have prepared metal monomethylcyclopentadienides $\text{CaCH}_3\text{C}_5\text{H}_4$, $\text{ZnCH}_3\text{C}_5\text{H}_4$, and $\text{CdCH}_3\text{C}_5\text{H}_4$ in a supersonic jet expansion and have recorded their electronic spectra using laser-induced fluorescence spectroscopy. A vibrational analysis of the first few low-lying electronic states of these organometallic molecules will be presented. This study represents the first gas-phase synthesis and spectroscopic observation of these half-sandwich free radicals.

Address of authors: Laser Spectroscopy Facility, The Ohio State University,
120 W. 18th Avenue, Columbus, OH 43210

RB6 (9:40)**A NEW LOOK AT AN OLD MOLECULE: THE VIBRONIC SPECTROSCOPY OF *p*-DIFLUOROBENZENE ($-\text{d}_4$)**Harry J. Elston, Fred G. Todd, and C.S. Parmenter

As a prelude to future studies of molecular dynamics, the vibronic supersonic jet spectroscopy of the $S_1(^1B_{2u}) \rightarrow S_0(^1A_g)$ transition of *p*-difluorobenzene- d_4 (pDFB- d_4) has been investigated for the lower 1600 cm^{-1} of the S_1 vibrational manifold. Dispersed single vibronic level fluorescence spectroscopy has been used to establish 12 S_1 fundamental frequencies. Significant spectroscopic differences from light pDFB occur. Two forbidden transitions not seen in the light molecule are observed, one being a second order Herzberg-Teller transition. Additionally, transitions with activity in a totally symmetric mode (ν_4) that is inactive in light pDFB dominate the vibronic spectra of pDFB- d_4 . We explore with Franck-Condon analysis the reasons why this fundamental is not seen in the light molecule.

Address of Elston and Parmenter: Department of Chemistry, Indiana University, Bloomington, IN 47405

Address of Todd: Department of Chemistry, Colorado State University, Ft. Collins, CO 80523

RB7 (9:57)

THE 614 nm SUPERSONIC JET SPECTRUM OF THIOACETALDEHYDE

D. C. Moule, H. Bascail, D. J. Clouthier, J. Karolczak, Y. G. Smeyers and A. Nino.

The $S_0 - T_1$ electronic transition in CH_3CHS , CD_3CHS , CH_3CDS , CD_3CDS has been observed in a continuous supersonic pyrolysis jet as a laser phosphorescence excitation spectrum. The potential surface for the torsional - wagging internal coordinates were mapped out with *ab initio* molecular orbital calculations with a 6-31G* basis in which the structural parameters were fully relaxed. The kinetic and potential energy data points were fitted to analytical double fourier expansions. These were incorporated into a two - dimensional Hamiltonian matrix in the torsion and wagging coordinates and symmetrized by the G_6 point group and solved for the energies and wavefunctions. The spectrum calculated from the the frequencies and Franck - Condon factors was fitted to the observed "hot" and cold band spectra and refinements were made to the potential surface.

Address of Moule and Bascail: Department of Chemistry, Brock University, St. Catharines, L2S3A1, Canada.

Address of Clouthier and Karolczak: Department of Chemistry, The University of Kentucky, Lexington, KY, 40506 - 0055

Address of Smeyers: Instituto de Estructura de la Materia, Consejo Superior de Investigaciones, C. Serrano 119 - 28006, Madrid, Spain

Address of Nino: Escuela Universitaria de Informatica, Universidad de Castilla - La Mancha, Ronda de Calatrava s/n, Ciudad Real, 13071, Spain.

Intermission

RB8 (10:25)

 AXIS-SWITCHING CORRECTIONS TO THE DUSCHINSKY EFFECT
 TAKAMASA MOMOSE AND JON T. HOUGEN

Early work on the Duschinsky effect¹ concentrated on relating vibrational modes in one electronic state to those in another by means of a simple rotation and translation in vibrational coordinate space:

$$x_i' = \sum_k a_{ik} x_k + C_i,$$

where the subscripts i and j range over the 3N-6 vibrational degrees of freedom. Because of the different equilibrium geometries in the two electronic states, however, the form of the Eckart conditions separating vibrational and rotational motion will be different. The consequences of this difference for rotational intensity distributions (assuming molecular shapes frozen at their equilibrium geometries in the two electronic states) has already been investigated (axis switching²). In the present talk we examine the consequences for Franck-Condon overlap integrals in electronic transitions of polyatomic molecules. Our treatment differs somewhat from a related investigation of Özkan³.

We have found that in general the indices i and j above must be augmented to include the three rotational degrees of freedom, in addition to the 3N-6 vibrational modes. The resulting formalism, when it is applied to condensed phases, remains almost unchanged from Duschinsky's original treatment, a result which is not surprising, since the three "rotational" degrees of freedom of the isolated molecule then become simply large-amplitude librational (i.e., special vibrational) modes. The resulting formalism is somewhat more difficult to apply to gas-phase high-resolution spectra since vibrational and rotational motions must be considered simultaneously. We are presently in the early stages of exploring the latter question, both algebraically and numerically, for various molecular geometries and geometry changes. The results of this investigation will be reported.

¹F. Duschinsky, Acta Physicochimica URSS, 7, 551-566 (1937).

²J. T. Hougen and J. K. G. Watson, Canad. J. Phys. 43, 298-320 (1965).

³I. Özkan, J. Mol. Spectrosc. 139, 137-162 (1990).

Address of Momose: Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan

Address of Hougen: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

RB9 (10:42)

ANALYSIS OF THE PHOTOLUMINESCENCE SPECTRA OF EXCHANGE-COUPLED Mo^{3+} PAIRS IN ONE-DIMENSIONAL LATTICES OF CsMgCl_2 AND CsCdBr_2
K. MARNEY, A. FRANCIS, G. MCPHERSON, P. MCCARTHY

High-resolution luminescence spectra of CsMgCl_2 doped with Mo^{3+} were found to contain bands that are very temperature sensitive between 5K and 2K and that can be assigned to exchange-coupled Mo^{3+} -V- Mo^{3+} pair-centers (V=divalent vacancy). When the lattice is doped with both Mo^{3+} and Li^+ , pair formation is inhibited and the spectra are principally those of the single Mo^{3+} cation. Well resolved multi-line luminescence spectra have been obtained from exchange-coupled Mo^{3+} pairs in the far red and near infrared. Both spectral regions reflected the ground state manifold splitting as calculated from EPR spectroscopy. The near IR luminescence region provided the best quantitative agreement between the optically observed ground state manifold and that calculated from the EPR data.

Address of Marney and Francis: Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109.

Address of McPherson: Department of Chemistry, Tulane University, New Orleans, Louisiana 70118.

Address of McCarthy: Department of Chemistry, Canisius College, Buffalo, NY 14208.

RB10 (11:59)

HIGH PRESSURE ODMR SPECTROSCOPY OF TRIPLET BENZOQUINONE SYSTEMS

J. L. BABER AND I. Y. CHAN

Optically Detected Magnetic Resonance (ODMR) experiments under pressures up to 35 kbar have been performed on p-benzoquinone (BQ) in dibromobenzene and neat BQ- d_4 . High pressures were obtained using a Merrill-Bassett diamond anvil cell. The microwave magnetic field was coupled to the sample by a carefully positioned hairpin loop.

The zero-field parameter D of BQ's lowest triplet state, $^3B_{1g} (n\pi^*)$, exhibited an enormous pressure sensitivity. Such a hypersensitivity to pressure has never been observed. This behavior is interpreted as originating from the vibronic interaction of a nearby (340 cm^{-1}) $^3n\pi^*$ state. A phase transition of BQ- d_4 was observed at 6 kbar.

Address of Baber and Chan: Department of Chemistry, Brandeis University, Waltham, Massachusetts, 02254.

RB11 (11:16)**Approximate Quantum Numbers
in the Optical Spectrum of NO₂****Stephen L. Coy and Kevin K. Lehmann**

The optical spectrum of NO₂ obtained in jet expansion fluorescence spectra by Persch et. al. [1], providing data on band origins shows a highly mixed spectrum with near-GOE level statistics, including level-repulsion. Microwave-detected microwave optical double resonance data obtained in our work [2], providing data on the distribution of levels at higher angular momentum, shows an ergodic spectrum with no detectable level repulsion. We examine the two data sets in the light of a multiple bright state model [3], and a related K-breakdown or weak-breakdown model. We find that the band origin data is consistent with a multiple bright state model with approximately 4 bright states mixed into each observed state. The high J data is consistent with the K-breakdown model in which Coriolis-coupling matrix elements are much smaller than the bright state - dark state vibronic interaction. An experimental test of this model is proposed. This indicates that the presence of approximately conserved quantum numbers in a molecular spectrum complicates the application of statistical measures of ergodicity.

1. G Persch, E Mehdizadeh, W Demtroder, Th Zimmermann, H Koppel, and LS Cederbaum, Ber. Bunsenges. Phys. Chem. **92**, 312(1988).
2. KK Lehmann, SL Coy, Ber. Bunsenges. Phys. Chem. **92**, 306(1988).
3. SL Coy, KK Lehmann, Phys. Rev. A **40**, 5935(1989).

Address of Coy: Massachusetts Institute of Technology, 18 Vassar Street Rm. 6-234B, Cambridge, Massachusetts 02139
 Address of Lehmann: Princeton University, Department of Chemistry, Washington Road, Princeton, New Jersey 08542

RB12 (11:33)**Tropyl (cyclo-C₇H₇) Radical Electronic States observed by Resonance Enhanced Multiphoton Ionization Spectroscopy****Russell D. Johnson III**

Two-photon electronic absorption spectra of the tropyl radical (cyclic C₇H₇) have been observed by Resonance Enhanced Multiphoton Ionization Spectroscopy (REMPI) from 415 to 590 nm, corresponding to 34000 to 48000 cm⁻¹. Two Rydberg series are assigned and an ionization potential determined: *np*, $\delta=0.35$; *nf*, $\delta=0.05$; IP=50177 cm⁻¹. Vibrational activity of the Rydberg states was observed and the frequencies were found to be similar to the ion: $\omega_2=862$ cm⁻¹ (ring breathing), $2\omega_{18}=1528$ cm⁻¹ (ring bending), and $2\omega_{20}=1284$ cm⁻¹ (CH out-of-plane bend).

Address: National Institute of Standards and Technology
 Chemical Kinetics and Thermodynamics Division
 Gaithersburg, Maryland 20899

RB13 (11:50)

MULTIPHOTON IONIZATION SPECTROSCOPY OF DIFLUOROMETHYL RADICALS

Jeffrey W. Hudgens, Russell D. Johnson III, Bilin P. Tsai, David V. Dearden, and
Sherif A. Kafafi

The structures and optical spectroscopy of the CHF₂ radical and cation were studied by *ab initio* molecular orbital calculations and by experiment. *Ab initio* calculations at the MP2/6-31G** theory level found that the optimum structure of the \tilde{X}^1A' CHF₂⁺ cation belongs to the C_{2v} point group with $r(C-F) = 1.2424 \text{ \AA}$, $r(C-H) = 1.0883 \text{ \AA}$, and $\angle F-C-F = 119.19^\circ$. The optimized structure of the ground state CHF₂ (\tilde{X}^1A') radical belongs to the C_s point group with $r(C-F) = 1.3360 \text{ \AA}$, $r(C-H) = 1.0843 \text{ \AA}$, $\angle F-C-F = 111.51^\circ$, and $\angle H-C-F = 113.65^\circ$. The *ab initio* angle between the F-C-F plane and the C-H bond is $\phi = 44.53^\circ$. Vibrational frequencies for each CHF₂ species were computed. The electronic spectra of CHF₂ and CDF₂ radicals were observed between 330-430 nm using mass resolved resonance enhanced multiphoton ionization (REMPI) spectroscopy. These spectra arose from two-photon resonances with planar Rydberg states. A third laser photon ionized the radicals. Spectroscopic constants were found for the \tilde{F}^3p Rydberg state of the CHF₂ radical ($\nu_{00} = 49312(10) \text{ cm}^{-1}$, ν'_1 (C-F str) = 1358(15) cm^{-1} , ν'_2 (CF₂ scissors) = 680(20) cm^{-1} , ν'_3 (OPLA) = 1022(8) cm^{-1}) and of the CDF₂ radical ($\nu_{00} = 49323(10) \text{ cm}^{-1}$, ν'_1 (C-F str) = 1300(15) cm^{-1} , ν'_2 (CF₂ scissors) = 650(15) cm^{-1} , ν'_3 (OPLA) = 864(13) cm^{-1}). The REMPI spectra exhibited $\nu''_1 = 1-5$ hot bands of the \tilde{X}^1A' radical. Modeling of these hot bands with a quartic double-well potential gives the inversion barrier, $B_{12} = 2800(500) \text{ cm}^{-1}$, and $\phi = 49(6)^\circ$.

Address of Hudgens, Johnson, Tsai, and Dearden:
Chemical Kinetics and Thermodynamics Division
National Institute of Standards and Technology
Gaithersburg, MD 20899

Address of Kafafi:
Department of Environmental Chemistry and Biology
Johns Hopkins University School of Hygiene and Public Health
615 North Wolfe Street
Baltimore, MD 21205

RC1 (8:30)

INTERACTION OF ROTATION AND LOCAL MODE TUNNELING IN OVERTONE SPECTRA OF XH_2 MOLECULES

K.K. Lehmann

It is now well established that the overtone spectra of most hydrides is dominated by transitions to states that are best described by the 'local mode' model where the vibrational energy is localized on a single X-H bond. For the case of exactly equivalent X-H bonds, this vibrational excitation tunnels between these bonds, leading to a lifting of the exact degeneracy of the different linear combinations corresponding to the irreducible representations (which are the eigenstates of the vibrational Hamiltonian). A model Hamiltonian that describes the effects of rotation of the local mode states will be discussed. In the limit where the tunneling frequency is much less than the rotational frequencies, the eigenstates of this Hamiltonian display the rotational structure consistent with the dynamically reduced symmetry of the molecule. For example a XH_4 molecule give a symmetric top spectrum. Further, tunneling must now reorient the rotational angular momentum (in the body fixed frame) as well as transfer the vibrational action. As a result, the rotation about the proper axes can dramatically slow the rate of tunneling.

Address of Lehmann: Department of Chemistry, Princeton University, Princeton, NJ 08544

RC2 (8:47)

POLARIZATION SPECTROSCOPY IN THE LIMIT OF STRONG SATURATION

Kevin K. Lehmann and Frank Spano

Polarization spectroscopy is one of the most sensitive methods of detection of Optical-Optical double resonance. It is based upon the differential population of the different M levels of the pumped state. As such one would expect that the strength of the signal would decrease in the limit of strong saturation. However, explicit solution of the coupled Maxwell-Block equations shows that if one has strong saturation and an optically thick sample, then one finds that as a result of pulse reshaping, the distribution of M level populations is even more strongly peaked than in the linear response limit, but of the opposite sense, i.e. for R branch lines the population peaks for $M \sim 0.9 J$ with a FWHM of only $\sim 0.25 J$.

Address of Lehmann: Department of Chemistry, Princeton University, Princeton, NJ 08544
Address of Spano: Department of Chemistry, Temple University, Philadelphia, Penn. 19122

RC3 (8:59)

PERTURBATIONS IN THE ν_1 AND $2\nu_1$ SPECTRA OF PROPYNE

E.R. Th. Kerstel, K.K. Lehmann, A. McIlroy, D.J. Nesbitt, B.H. Pate, and G. Scoles

High resolution, molecular beam spectra of the fundamental and first overtone of the acetylenic C-H stretch in propyne have been obtained in a warm expansion (35 K). Both spectra are perturbed. The fundamental has an anomalous K structure due to a distant perturber. This K structure is exactly reproduced at each value of J. The assignment of the perturber involves calculation of the spectroscopic constants using the SPECTRO program. The appearance of the overtone spectrum is qualitatively different. Here we observe many weak, local perturbations to the spectrum. Deconvolution of the spectrum provides information on the coupling of the C-H stretch to the bath states. The overtone spectrum thus provides insight into process of intramolecular vibrational energy redistribution (IVR)

Address of McIlroy and Nesbitt: Joint Institute for Laboratory Astrophysics, University of Colorado and National Institute of Standards and Technology, and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0440.

Address of Kerstel, Lehmann, Pate and Scoles: Department of Chemistry, Princeton University, Princeton, NJ 08544.

RC4 (9:16)

DOES A HEAVY CENTRAL ATOM REDUCE THE RATE OF VIBRATIONAL ENERGY RELAXATION ?

E.R. Th. Kerstel, K.K. Lehmann, T.F. Mentel, B.H. Pate, and G. Scoles

We have used high resolution infrared spectroscopy to study the IVR process in the series of molecules $(\text{CH}_3)_3\text{X}-\text{C}\equiv\text{C}-\text{H}$ ($\text{X} = \text{C}, \text{Si}, \text{and Sn}$). Our optothermal spectrometer is interfaced with two color center lasers that allow us to obtain both the fundamental and first overtone spectra of the acetylenic C-H stretch. All six spectra show homogeneously broadened lines. The width of the Lorentzian lineshapes corresponds to the lifetime of the initial vibrational excitation of the C-H stretch. In the fundamental we find that the linewidth decreases as the mass of the central atom increases suggesting that a heavy atom does inhibit IVR. The homogeneous lifetime is about 200 ps in the carbon species and increases to about 6 ns in the tin compound. However, a simple mass effect cannot fully explain the measured linewidths in both the fundamental and overtone. Other possible explanations of the data will be presented.

Address of Kerstel, Lehmann, Mentel, Pate, and Scoles: Department of Chemistry, Princeton University, Princeton, NJ 08544.

RC5 (9:33)

STUDY OF ENHANCED IVR IN MOLECULES WITH HINDERED INTERNAL ROTATION USING HIGH RESOLUTION INFRARED SPECTROSCOPY

E.R. Th. Kerstel, K.K. Lehmann, T.F. Mentel, B.H. Pate, and G. Scoles

Using an optothermal molecular beam spectrometer we have measured the ν_1 and $2\nu_1$ spectra of several terminal acetylenes. We have studied a series of small acetylenes, propynal, 3-fluoropropynal, and vinyl acetylene, where the density of states increases through the series. These spectra show numerous weak, local perturbations characteristic of the IVR process. From these assigned spectra we can determine the homogeneous lifetime of the initial vibrational excitation. We have also attempted to record the spectra of the methyl substituted compounds butynone and 3-methyl butenyne, related to the previous compounds by placing a methyl group on the third carbon. In the fundamental region of ν_1 we observe no spectrum, indicating that the IVR lifetime is decreased by the addition of the methyl group. We are, however, able to obtain a spectrum in the ethylene region of 3-methyl butenyne suggesting that these vibrations are more resistant to the IVR rate increase brought about by the addition of the methyl group.

Address of Kerstel, Lehmann, Mentel, Pate, and Scoles: Department of Chemistry, Princeton University, Princeton, NJ 08544.

RC6 (9:50)

ROTATIONALLY RESOLVED, MOLECULAR BEAM, OVERTONE SPECTROSCOPY OF HYDROGEN-BONDED COMPLEXES: $2\nu_1$ OF $(\text{HCN})_2$ AND HCN-HF

E.R.Th. Kerstel, T.F. Mentel, B.H. Pate, and G. Scoles

We have used a 1.5 μm color-center laser, with the optothermal detection method, to study the vibrational predissociation in the $2\nu_1$ bands of HCN dimer and HCN-HF.

For HCN dimer the complexation-induced redshift of $-6.3923(5) \text{ cm}^{-1}$ is nearly exactly equal to twice the fundamental redshift, indicating a very small (0.1 %) increase in the anharmonicity of the CH stretch potential. However, the much smaller than twice the fundamental redshift ($-1.2905(5) \text{ cm}^{-1}$), observed in the overtone of HCN-HF, indicates a relatively large (1 %) decrease in the anharmonicity. The linewidths of the HCN dimer spectrum are instrument limited, giving a lower limit of 11 ns to the lifetime. The upper limit is given by the 90 μs time-of-flight from laser crossing to detector. In the case of HCN-HF we find linewidths broader than the 22 MHz instrumental width. The homogeneous contribution to the overall linewidth is roughly 15 MHz, which compares to a 9.9 MHz Lorentzian component that was needed to fit the fundamental transitions. Presently, efforts are underway to measure the overtone linewidths at improved resolution.

Address of Kerstel, Mentel, Pate, and Scoles: Department of Chemistry, Princeton University, Princeton, NJ 08544.

Intermission

RC7 (10:25)

RE-EXAMINATION OF THE ELECTRONIC SPECTRUM OF HCP

M.A. Mason and K.K. Lehmann

In 1969, Johns et al published an extensive study of the electronic spectrum of HCP and DCP in the near UV. We are in the process of re-examining this spectrum using pulsed dye laser excitation and fluorescence detection in a pulsed jet apparatus. This work has demonstrated that there is an abrupt cut off of fluorescence near 41600 cm^{-1} , which we interpret as due to predissociation on the ground electronic surface. The spectrum shows a density of perturbations throughout the singlet systems that indicate substantial mixing with the still sparse S_0 levels. The spectrum in the region a few thousand wavenumbers below dissociation is very rich, with about 3 times the number of bands as a harmonic estimate of the total density of S_1 and S_2 vibrational levels. Most of the levels are unassigned, though it is clear that the origin of the "C" state (now known to be S_2) is well below the earlier estimate. We plan Zeeman quantum beat measurements which we hope will aid in assignment.

Address of Mason and Lehmann: Department of Chemistry, Princeton University, Princeton NJ 08544

RC8 (10:42)

VIBRONIC STRUCTURES AND PREDISSOCIATION DYNAMICS OF TRIATOMIC CLUSTER HgAr_2
M. OKUNISHI, K. YAMANOUCHI, AND S. TSUCHIYA

An HgAr_2 triatomic cluster was investigated by the measurement of laser induced fluorescence spectra of the $\tilde{A}-\tilde{X}$ and $\tilde{B}-\tilde{X}$ transitions and optical-optical double resonance spectra of the $\tilde{E}-\tilde{A}$ transitions. The fundamental wavenumbers were determined to be $\omega_1 = 26.1$, $\omega_2 = 11.9$, and $\omega_3 = 28.4 \text{ cm}^{-1}$ for the \tilde{A} state and $\omega_1 = 23.6$ and $\omega_2 = 10.1 \text{ cm}^{-1}$ for the \tilde{B} state. A large amplitude motion of one Ar atom with respect to an HgAr^+ ion core was proposed as a characteristic vibrational motion in the lowest Rydberg \tilde{E} state based on the fundamental wavenumbers of $\omega_1 = 102$ and $\omega_2 = 5 \text{ cm}^{-1}$.

The predissociation process in the B state, $\text{HgAr}_2(\tilde{B}) \rightarrow \text{HgAr}(\tilde{A}) + \text{Ar}$, was also investigated. Using the vibrational state distribution of the HgAr fragment in the A state, the dissociation energies of HgAr_2 to $\text{Hg} + \text{Ar} + \text{Ar}$ were derived to be 367, 533, and 247 cm^{-1} for the \tilde{X} , \tilde{A} , and \tilde{B} states, respectively.

Address of Okunishi: Institute for Molecular Science, Okazaki 444, Japan

Address of Yamanouchi, and Tsuchiya: Department of Pure and Applied Sciences, College of Arts and Sciences, The University of Tokyo, Meguro-ku, Tokyo 153, Japan

RC9 (10:54)

LASER PHOTOELECTRON INVESTIGATION OF JET-COOLED 1,4-DIFLUOROBENZENE.
John P. Lucia, Xinbei Song, James P. Reilly.

Laser photoelectron spectra of jet cooled p-difluorobenzene have been obtained using nanosecond and picosecond ionization pulses. Previously unobserved vibrational levels of the $^2B_{2g}$ ion ground state have been recorded.

Picosecond pulses have been used with pump - probe multiphoton ionization techniques and laser photoelectron spectroscopy to study the dynamics of the $^1B_{2u}$ lowest excited state in p-difluorobenzene. Vibrational levels have been studied including several shown previously to exhibit intramolecular vibrational redistribution (IVR), as well as identifiable Fermi resonance states both above and below the reported IVR threshold.

Address: Department of Chemistry, Indiana University, Bloomington, IN 47405.

RC10 (11:06)

TWO-COLOR PICOSECOND PHOTOELECTRON STUDY OF IVR IN ALKYLANILINE AND
ALKYLBENZENE MOLECULES

Xinbei Song, John P. Lucia and James P. Reilly

Time dependent intramolecular vibrational relaxation (IVR) in the 1B_2 excited electronic state of alkyraniline and alkylbenzene molecules was directly monitored by employing a two-photon ionization process. Photoelectrons were produced by two-color pump-probe ionization induced by picosecond laser pulses impinging on a jet-cooled molecular beam. Their kinetic energies of photoelectrons were measured by a time of flight method. With the picosecond pump laser tuned to different vibrational modes in the excited electronic state of these molecules and the probe laser adjusted to the different delay times, photoelectron spectra were recorded. The extended chain conformation (trans) and the coiled chain conformation (gauche) exhibit remarkably different IVR behavior. Comparison of the rates of IVR in these molecules will be made. The conformational dependence of the ionization potential in these molecules will also be discussed.

Address: Department of Chemistry, University of Indiana, Bloomington, IN 47405

RC11 (11:18)

ADVANCES IN LOW TEMPERATURE PHOTOACOUSTIC SPECTROSCOPY; METHANE'S $\Delta v=4$ OVERTONE
K. BORRAS, J. P. REILLY.

Experiments designed to simplify methane's overtone spectrum as observed with a photoacoustic spectrometer have been performed.

A Schwartz Ti:Sapphire laser operating in the ring configuration (approximate linewidth 0.001 cm^{-1}) was tuned via an intracavity scanning etalon and galvoplete assembly. Positioned within the laser cavity was a newly designed cryostatically cooled photoacoustic cell. This cell was capable of cooling the methane sample to liquid nitrogen temperatures with no window warming effects.

High resolution low temperature photoacoustic spectra were recorded within a small region of the $v_1 + 3v_4$ methane overtone centered at 11629 cm^{-1} . Near doppler limited linewidth (0.022 cm^{-1}) and reduced rotational spectral congestion were observed.

Address: Department of Chemistry, Indiana University, Bloomington, IN 47405

RC12 (11:30)

PHOTOACOUSTIC OVERTONE SPECTROSCOPY OF PROPENE
ZHEN LIN AND J.P. REILLY

The vibrational third overtone spectrum of the acetylenic C-H stretch of propyne was obtained by intracavity photoacoustic spectroscopy with a resolution limited by room temperature Doppler broadening and pressure broadening. Comparing the experimental spectrum with symmetric top simulation, it was found that all the peaks in the P and R branches match quite well within the measurement precision of 0.02 cm^{-1} when J is larger than 10. However, for J less than 10, extra peaks appeared in the experimental spectrum. In addition, deviation of positions of peaks from simulation was found. A possible explanation is that the transitional upper state is perturbed. It was possible to assign all peaks. But some features of the spectrum have not yet been explained.

Address: Department of Chemistry, Indiana University, Bloomington, IN 47405.

RC13 (11:42)

INVESTIGATION OF DCL STRETCHING VIBRATIONS IN HYDROGEN BOND
DIMERS

Z. Wang and J. W. Bevan

A diode laser cw supersonic jet spectrometer has been used to investigate vibrations in the DCl stretching fundamental frequency regions in tetratomic and pentatomic hydrogen bond dimers. Results will be reported for $\text{N}_2\text{--DCl}$, OC--DCl , $\text{CO}_2\text{--DCl}$ and DCN--DCl . Where appropriate the experimental results will be correlated with predictions based on theoretical calculation.

Chemistry Department, Texas A&M University, College Station, Texas 77843

RE1 (1:30)**SUBMILLIMETER MICROWAVE SPECTROSCOPY
IN GORKY, USSR: CURRENT RESEARCH**

Invited Paper. 30 min.

A. F. KRUPNOY, Applied Physics Institute, USSR Academy of Science,
Gorky, USSR 603600.**RE2 (2:03)****MILLIMETER AND SUBMILLIMETER SPECTRUM OF HIGHLY EXCITED STATES OF WATER
J. C. PEARSON, T. J. ANDERSON, E. HERBST, AND F. C. DE LUCIA**

Although only a few transitions of water have significant absorption strengths at ambient temperatures in the millimeter and submillimeter spectral region, a number of additional transitions are observable in more highly excited sources. Perhaps the most significant of these are in astronomical sources, a number of which may be associated with interstellar masers.¹ This is extremely fortunate because although astronomical water sources are ordinarily difficult to observe because of atmospheric attenuation, these highly excited transitions have no systematic relation to the absorptions in the ambient atmosphere. In this paper we report the observation of a number of such transitions in the ground as well as 010, 020, 100 and 001 vibrations states.

¹K. M. Menton, G. J. Melnick, and T. G. Phillips, *Ap. J. (Letters)* **350**, L41 (1990).

Address of Pearson and De Lucia: Department of Physics, 174 W. 18th Avenue, The Ohio State University,
Columbus, OH 43210.Address of Herbst: Department of Physics, Duke University, Durham, NC 27706.Address of Anderson: Department of Chemistry, Physical Sciences, Bdg. 1, UC Irvine, Irvine CA 92717.**RE3 (2:20)****CYCLOPROPANE-SULFUR DIOXIDE. MICROWAVE SPECTRUM AND STRUCTURE
A. M. ANDREWS, K. W. HILLIG II, AND R. L. KUCZKOWSKI**

The microwave spectrum of the cyclopropane-sulfur dioxide van der Waals complex has been observed by Fourier transform microwave spectroscopy. The spectrum exhibited *a*- and *c*-dipole selection rules; the *c*-type transitions were split into doublets of unequal intensity separated by about 200 kHz. The stronger and weaker *c*-type transitions were each fit independently with the *a*-type transitions using the Watson S-reduced Hamiltonian to rotational constants $A = 6176.635(7)$ MHz, $B = 1258.497(1)$ MHz, $C = 1180.101(1)$ MHz for the stronger transitions and $A = 6176.828(8)$ MHz, $B = 1258.497(1)$ MHz, $C = 1180.101(1)$ MHz for the weaker transitions. The complex has C_s symmetry. The C_2 axis of sulfur dioxide lies in the CCC plane nearly parallel to a C-C bond with the oxygens straddling the plane; the center of mass of the sulfur dioxide is 3.31 Å from the C-C bond center. The splittings in the spectrum suggest an internal rotation of the cyclopropane subunit.

Address: Department of Chemistry, University of Michigan, 930 N. University Ave., Ann Arbor, Michigan 48109, U.S.A.

RE4 (2:32)

CYCLOPROPANE-WATER: MICROWAVE SPECTRUM AND STRUCTURE A. M. ANDREWS, K. W. HILLIG II, AND R. L. KUCZKOWSKI

The microwave spectrum of the cyclopropane-water complex has been observed by Fourier transform microwave spectroscopy. Only a -type transitions were observed in the spectrum; they were split into doublets of unequal intensity separated by 0.5 to 2 MHz. The stronger and weaker transitions were fit separately to rotational constants $A = 19950(100)$ MHz, $B = 2158.845(5)$ MHz, $C = 2340.321(5)$ MHz and $A = 19945(160)$ MHz, $B = 2158.843(7)$ MHz, $C = 2340.876(7)$ MHz, respectively. The water is hydrogen bonded to the center of an edge of the cyclopropane; the hydrogen bond is nearly linear (bond center-H-O angle = $180(5)^\circ$) with the O and bonded H in the CCC plane. The H to edge distance is 2.35 Å. The position of the free H is uncertain. Nuclear spin statistics and isotopic data indicate that the splittings in the spectrum arise from an internal motion of the water subunit which exchanges the two hydrogens.

Address: Department of Chemistry, University of Michigan, 930 N. University Ave., Ann Arbor, Michigan 48109, U.S.A.

RE5 (2:44)

INVESTIGATIONS OF LINE BROADENING AND LINE SHIFT PARAMETERS IN LOW J ROTATIONAL TRANSITIONS OF CARBON MONOXIDE.

S. P. BELOV, M. YU TRETYAKOV, AND R. D. SUENRAM

The $J=2-1$, $3-2$, and $4-3$ rotational transitions of CO have been measured using the RAD1 microwave spectrometer at the Applied Physics Institute in Nizhny Novgorod. The pressure shift and broadening parameters were measured for the $J=2-1$ and $3-2$ transitions. This was done with CO (self broadening) and CO₂ (foreign gas broadening). The unperturbed transition frequencies are believed to be accurate to two kilohertz. These improved frequency measurements should be useful in planetary atmosphere research. Details of the experimental results will be presented.

Address of Belov and Tretyakov : Institute of Applied Physics, Nizhny Novgorod, USSR.
Address Suenram : Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

RE6 (2:56)

PRESSURE BROADENING OF WATER BETWEEN 80 K AND 600 K

T. M. GOYETTE, J. M. DUTTA, C. R. JONES, and F. C. DE LUCIA

The results of recent experiments of water pressure broadened by O₂, N₂, He, and H₂ will be presented. The $3_{1,3}-2_{2,0}$ and $4_{1,4}-3_{2,1}$ transitions of water (H₂O) were studied between 80 K and 600 K. Results for the temperature dependence of the pressure broadening parameters are compared with predictions from theory and with previous experimental results. Low temperature measurements were made in a collisionally cooled cell¹ with a continuously variable temperature between 80 K and 300 K. Static measurements were made in a quartz cell enclosed in an oven with a continuously variable temperature between 80 K and 600 K.

¹ T. M. Goyette and F. C. De Lucia, *J. Mol. Spectrosc.* **143**, 346 (1990).

Address of Goyette and De Lucia: Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106.

Address of Dutta and Jones: Department of Physics, North Carolina Central University, Durham NC 27707.

Intermission

RE7 (3:27)

THE GROUND TORSIONAL STATE OF ACETALDEHYDE.

I. KLEINER, J. T. HOUGEN, R. D. SUENRAM, F. J. LOVAS AND M. GODEFROID.

New microwave measurements on the ground state of acetaldehyde have been carried out using a Fourier transform microwave spectrometer in the region of 7 to 26 GHz (typical measurement uncertainty 4 kHz), and a conventional Stark spectrometer in the region from 45 to 116 GHz (uncertainty: 40 kHz). These new ground state measurements and remeasurements have permitted a much better fit, using two theoretical models, of a data set containing far-infrared combination differences from the literature, microwave transitions from the literature and the new microwave transitions measured in this work. The root-mean-square residuals obtained are only slightly larger than the estimated measurement accuracy. The first theoretical model is a high-barrier effective Hamiltonian for one vibrational state only, based on Fourier expansions in terms of the form $\cos(2\pi/3)(\rho K - \sigma)$. The second model is based on calculations using an internal-rotation potential function. The present successful fits using either model indicate that earlier fitting problems using the second model were caused by problems in the original microwave data set, rather than by problems inherent to the model, at least for the ground torsional state of acetaldehyde. Similar techniques are now being tried in order to fit simultaneously the ground torsional state ($v_t=0$), the first excited torsional state ($v_t=1$) and far-infrared transitions from the literature ($v_t=1-0$).

Address of Kleiner, Hougen, Suenram and Lovas : Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA.

Address of Godefroid : Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles, CP160, 50 av. F-D. Roosevelt, 1050 Bruxelles.

RE8 (3:44)

AN INVESTIGATION OF THE MICROWAVE SPECTRUM AND MOLECULAR STRUCTURE OF SULFONYL CHLORIDE ISOCYANATE

OKSIK JO, F. J. LOVAS, R. D. SUENRAM AND JACK D. GRAYBEAL

An electron diffraction study¹ of sulfonyl chloride isocyanate, SO_2ClNCO , could not make a definitive choice between the system being a single isomer with an SCl-NC dihedral angle of 94° or a mixture of two isomers having angles of 71° and 110° . The microwave spectrum of SO_2ClNCO has been investigated between 7 GHz and 26 GHz using both a conventional Stark spectrometer and a Fourier transform spectrometer. The spectra of two isotopic species (^{35}Cl and ^{37}Cl) were assigned and the rotational constants and the nuclear quadrupole coupling constants for ^{35}Cl , ^{37}Cl and ^{14}N were determined. Using the six rotational constants derived from the assignment and parameters relating the $-\text{SO}_2$ moiety structure from the electron diffraction study and other studies of molecules containing the SO_2 group, the dihedral angle was found to be $93.86^\circ(12)$ and the $\angle\text{NCO} = 175.68(6)$. This study indicates the existence of only a single isomer at the temperature of the Fourier spectrometer experiment and a nonlinearity of the NCO group as has been observed in other similar systems. The value obtained for ^{35}Cl , $\chi_{\text{ZZ}} = -71.6$ MHz indicates a S-Cl bond ionicity of 35%.

¹ Brunvall, J. and I. Hargittai, J.C.S. Dalton, 299 (1978).

Address of Jo and Graybeal: Dept. of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0212.

Address of Lovas and Suenram: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

RE9 (4:01)

MICROWAVE SPECTRA OF MONOHALOGENATED ALLENES: CHLOROALLENE, BROMOALLENE, AND IODEALLENE TERUHIKO OGATA AND YUZURU NIIDE

The microwave spectra of $\text{ClHC}=\text{C}=\text{CH}_2$, $\text{BrHC}=\text{C}=\text{CH}_2$, and $\text{IHC}=\text{C}=\text{CH}_2$ have been studied by a conventional Stark modulation spectrometer. The rotational constants in A, B, and C in a vibrational ground state were determined from both a- and b-type transitions frequencies.

The nuclear quadrupole coupling constants χ_{aa} , χ_{bb} , χ_{cc} , and χ_{ab} for chlorine, bromine, and iodine have been determined from the hyperfine splittings. The molecular structures which reproduce the observed moments of inertia were obtained under the reasonable assumptions.

Systematic changes among the structural parameters in the series of monohalogenated allenes, $\text{XHC}=\text{C}=\text{CH}_2$ (X = H, F, Cl, Br, and I) were observed. The bond lengths and the quadrupole coupling constants for halogenated ethenes, allenes, and ethanes, revealed that the double bond in allenes has more single bond character than that in ethenes.

Address of Teruhiko Ogata: Faculty of Liberal Arts, Shizuoka University, Shizuoka 422 Japan.

Address of Yuzuru Niide: Department of Mathematics and Physics, National Defense Academy, Yokosuka 239 Japan.

RE10 (4:13)

ROTATIONAL AND VIBRATIONAL COLLISIONAL PROCESSES IN CH_3Cl

T. W. PAPE, F. C. DE LUCIA, D. D. SKATRUD

The rates of several collisional processes have been measured in CH_3Cl using time-resolved infrared/mm-wave double resonance. This study was performed to characterize further collisional energy transfer processes found in other methyl halides previously studied at Duke: $^{13}\text{CH}_3\text{F}$ and $^{12}\text{CH}_3\text{F}$.

A process was discovered¹ in CH_3F that thermalizes rotational levels of the same symmetry type within a vibrational state. The cross section for this process is large enough that it makes a significant contribution to the pressure broadened linewidth. This process has been observed to have a very large cross section in CH_3Cl . Fundamental energy conservation considerations place constraints on the range of states that can be thermalized by this process. CH_3Cl data which addresses this issue will be presented and discussed. In addition, our previous work in CH_3F showed a large vibrational swapping rate which effectively circumvented the $\Delta K=3n$ selection rule. This rate is expected to be much smaller in the pumped vibrational state of CH_3Cl due to the smaller vibrational transition moment. This has been quantitatively confirmed by our CH_3Cl measurements.

¹ H. O. Everett and F. C. De Lucia, *J. Chem. Phys.* **90**, 3520 (1989).

Address of Pape: Department of Physics, Duke University, Durham, NC 27706

Address of De Lucia: Department of Physics, Ohio State University, Columbus, OH 43210

Address of Skatrud: U.S. Army Research Office, Research Triangle Park, NC 27709

RE11 (4:30)

DIELECTRIC RELAXATION SPECTRA OF T-BUTYL ALCOHOL-WATER MIXTURE USING TIME DOMAIN REFLECTOMETRY A.C.KUMBHARKHANE, S.M.PURANIK, AND S.C.MEHROTRA

Dielectric relaxation measurements in the frequency range of 10 MHz-10 GHz have been carried out in t-butyl alcohol-water mixtures with various concentrations over the temperature range 273 K - 313 K using a time domain reflectometry (TDR) method.

The bilinear calibration method as suggested by Cole¹ as been used to correct the permittivity spectra. The corrected spectra can be fitted with a single relaxation time with small amount of Cole-Davidson behaviour. Deviations from ideal mixing behaviour in permittivity parameter ($\epsilon_\infty - \epsilon_0$) and relaxation time (τ) suggested formation of the polymeric structure in t-butyl alcohol-water mixtures.

The dielectric relaxation behaviour shows the same structural changes as observed in ultrasonic relaxation. However, the maxima in excess permittivity and excess relaxation time occur at different positions. This can not be explained by simple model of the polymeric structure.

¹R.H.Cole, J.G.Berberian, S.Mashimo, G.Chryssikos, A.Burns and E.Tombari, J.Appl.Phys. **88**(2), 793(1989).

²M.Tabellout, P.Lanceleur, J.R.Emery, D.Hayward and R.A.Pethrick, J.Chem. Soc. Faraday Trans. **88**(9), 1493(1990).

Address of Kumbharkhane, Puranik and Mehrotra: Department of Physics, Marathwada University, Aurangabad, 431 001 India.

RE12 (4:42)

TUNNELING INTERACTIONS BETWEEN DIFFERENT CONFORMERS IN VIBRATIONALLY EXCITED STATES OF ETHYLPHOSPHINE, $\text{CH}_3\text{CH}_2\text{PH}_2$

P. Groner and J. R. Durig

The microwave spectra of several vibrationally excited states of both the *trans* and *gauche* conformers of ethylphosphine have been assigned and analyzed. Most transitions assigned to the *gauche* conformer are split into two or four components. The larger splittings result from tunneling through the barrier between the equivalent *gauche* forms. They have been analyzed with an effective Hamiltonian for two states with Coriolis interaction. Energy differences of 229.4, 51 and 6.52 MHz between the symmetric and antisymmetric $J=0$ levels have been obtained for the first vibrationally excited states of the C-PH₂ torsion, the C-CH₃ torsion and the CCP bending vibration, respectively. The smaller splittings are due to methyl group internal rotation for which a barrier of 1050 cm⁻¹ has been determined from the excited state of the C-CH₃ torsion. An additional perturbation is present in the $J_{3,1,2}-J_{2,1,2}$ interstate transition series of these excited states. In the case of the C-PH₂ torsional excited state, it is caused by a Coriolis-type interaction through the *gauche-trans* barrier with a vibrationally excited state of the *trans* conformer whose $J=0$ level is 1.24 or 1.59 cm⁻¹ above the antisymmetric $J=0$ *gauche* state.

Address: Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208, USA

RE13 (4:59)

A PHYSICAL INTERPRETATION OF THE TUNNELING PARAMETERS IN THE INTERNAL AXIS TYPE TREATMENT OF LARGE AMPLITUDE MOTIONS

P. Groner

A straightforward approach is used to outline solutions of the general rotation-internal rotation Hamiltonian

$$H = \frac{1}{2} (\tilde{\omega} \dot{\tau}) \begin{pmatrix} I(\tau) & I'(\tau) \\ \tilde{I}'(\tau) & I_{\tau}(\tau) \end{pmatrix} \begin{pmatrix} \omega \\ \dot{\tau} \end{pmatrix} + V(\tau)$$

in terms of a product basis from symmetric rotor eigenfunctions and exponential functions. The solutions of the zero-order Hamiltonian

$$H_0 = (p_{\tau} - P_Z \rho_0) F(t) (p_{\tau} - \rho_0 P_Z) + V(\tau)$$

are discussed in some detail. They are used to derive localized state functions. The matrix elements of the full Hamiltonian are then written in terms of the zero-order solutions and the localized functions. This leads to an interpretation for the tunneling parameters used in effective Hamiltonians to explain the spectra of molecules with large amplitude motions. The generalizations necessary to treat multidimensional problems are discussed.

Address: Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208, USA

RF1 (1:30)

A SIMULATION OF THE ν_4 BAND OF CHLORINE NITRATE

K. P. Carten and R. W. Lovejoy

The ν_4 band of chlorine nitrate has been found in the earth's stratosphere and is therefore of particular interest concerning the depletion of ozone over Antarctica. An asymmetric rotor program was implemented to generate synthetic spectra of this band. A comparison of the synthetic and experimental spectrum of the ClONO_2 ν_4 band will be discussed.

Address of Carten and Lovejoy: Department of Chemistry, Lehigh University, Bethlehem, PA 18015

RF2 (1:42)

HIGH RESOLUTION FT-IR SPECTROSCOPY OF *TRANS*-1,2-DIFLUOROETHYLENE- d_2

NORMAN C. CRAIG, STEPHEN C. STONE AND WALTER J. LAFFERTY

A complete structure of *trans*-1,2-difluoroethylene, which is a non-polar molecule, would assist in interpreting the surprisingly greater energy of this isomer in comparison with its *cis* isomer.¹ We are in the process of obtaining high resolution (0.004 cm^{-1}) spectra of several bands of three isotopomers of this near-symmetric prolate top molecule with the goal of finding precise ground state rotational constants and a reliable " r_0 " structure. Last year we reported an analysis of three bands in the spectrum of the d_0 species.² This year, we report on the preliminary analysis of two bands in the spectrum of the d_2 species.

From the A-type band at 1176 cm^{-1} which is due to antisymmetric CF stretching, $\nu_{10}(\text{b}_u)$,³ we obtain initial values of B" and C" equal to $0.134021(5) \text{ cm}^{-1}$ and $0.121108(5) \text{ cm}^{-1}$. The higher K levels of this band are slightly perturbed, but a set of upper state constants can be obtained by fitting all observed transitions through $K = 6$. The two ground state constants are in good agreement with values calculated from geometric parameters in which the CCF bond angle and CF bond length were fit to moments of inertia for the d_0 species while fixing other parameters to those transferred from the *cis* isomer. In the *trans* isomer, the CCF bond angle is smaller, and the CF bond length is longer.

In addition, the A/B-hybrid band at 1331 cm^{-1} has been examined. This band, which is due to the combination tone, $\nu_7(\text{a}_u) + \nu_8(\text{b}_g)$,³ is heavily perturbed. The A-type Q-branch is split into two strong components separated by 1 cm^{-1} .

¹S. Saebe and H. Sellers, J. Phys. Chem. **92**, 4266 (1988)

²N. C. Craig, D. W. Brandon and W. J. Lafferty, Forty-Fifth Symposium on Molecular Spectroscopy, Columbus, OH, MF11

³N. C. Craig and J. Overend, J. Chem. Phys. **51**, 1127 (1969).

Address of Craig and Stone: Department of Chemistry, Oberlin College, Oberlin, OH 44074

Address of Lafferty: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

RF3 (1:59)

PERFORMANCE OF A TUNABLE DIODE LASER SYSTEM WHICH UTILIZES ALL REFLECTIVE OPTICS

J. BALENT, A. W. MANTZ

This preliminary work describes the performance characteristics of a Tunable diode laser (TDL) system which incorporates diamond turned off axis parabolic mirrors throughout the system. The TDL is wavelength stabilized by a spherical Fabry-Perot which in turn is locked to the fringe of a single mode stabilized HeNe laser. The etalon may be scanned under computer control with the TDL locked to the etalon fringe.

Preliminary data on carbon dioxide and acetylene will be presented

Address of Balent and Mantz: Department of Physics, Franklin and Marshall College, P. O. Box 3003, Lancaster, PA 17604-3003.

RF4 (2:11)

DATA ACQUISITION SYSTEM FOR DIODE LASER KINETIC SPECTROSCOPY AND APPLICATIONS TO HOCO AND ETHYL RADICALS

PHILIP M. JOHNSON, WAFAA M. FAWZY AND TREVOR J. SEARS

We have developed a new data acquisition system for diode laser spectrometers used to measure spectra of transient molecules formed photolytically using a pulsed laser. The new system employs a novel segmented reflective chopper wheel whose rotation is synchronized to the photolysis laser firing. The wheel splits the time between photolysis laser shots into four slices and three spatially separate beams which measure (i) the transient sample of interest (ii) a reference gas spectrum and (iii) an étalon spectrum. The three beams are recombined on the element of a single detector, amplified and passed to a CAMAC programmable transient recorder controlled by a PC. We are able to measure the sample, reference and étalon spectra and the I_0 level on every laser shot thereby improving both the speed and accuracy of the measurements. We illustrate the results by reference to new spectra of the HOCO and ethyl radicals.

Address of Johnson: Department of Chemistry, State University of New York, Stony Brook, NY 11794.

Address of Fawzy and Sears: Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973.

RF5 (2:28)

SPECTRA OF ^{13}C ENRICHED CO_2 AT ELEVATED TEMPERATURES IN THE $15\ \mu\text{m}$ REGION

MARK P. ESPLIN AND MICHAEL HOKE

The GL (Air Force's Geophysics Laboratory) high resolution Fourier transform spectrometer has been used to measure spectra of a ^{13}C enriched sample of CO_2 heated to 800K in a high temperature absorption cell. The single pass cell had an absorption path of 1.75 meter, where the central 1 meter section of the cell was maintained at 800K and a temperature gradient was present in the two end sections. The enriched sample consisted of 88% $^{13}\text{C}^{16}\text{O}_2$, 11% $^{13}\text{C}^{18}\text{O}^{16}\text{O}$, and 1% various other isotopes. Results of the line position analysis will be presented at the Symposium.

This work was supported by the Air Force Office of Scientific Research (AFOSR) as part of GL Task 2310G1.

Address of Esplin: Stewart Radiance Laboratory, Utah State University, 139 The Great Road, Bedford, Ma 01730.

Address of Hoke: Geophysics Laboratory (AFSC)/OPS, Hanscom AFB, Bedford, Ma 01730.

RF6 (2:40)

INTENSITY AND POSITION MEASUREMENTS OF CARBON DIOXIDE LINES IN THE 4370 TO 4640 cm^{-1} REGION

L.P. GIVER AND C. CHACKERIAN, JR.

A set of 14 spectra of the carbon dioxide absorption bands in the 4300 to 4700 cm^{-1} region were obtained with a BOMEM DA3.002 FTS and a White cell using absorption path lengths between 507 and 1307 meters. The principal purpose of this work was to make the first laboratory measurements of the transition moment and Herman-Wallis intensity parameters of the $^{12}\text{C}^{16}\text{O}_2$ (3110)_{IV} - (0000) band at 4416.15 cm^{-1} . This weak band was recently found to be prominent in the thermal emission spectrum of the dark side of Venus¹. Our measured rotationless transition moment of this band is $R^2 = (1.41 \pm 0.14) \times 10^{-11}$ Debye². Line positions for this band were calibrated using the 2-0 band² of CO. The spectra of CO and CO₂ were recorded simultaneously with a small amount of added CO to the CO₂.

In this spectral region we have also recorded data which is suitable for intensity and positional work on the (3110)_{III} - (0000), (3220)_{III} - (0110) and (4000)_{IV} - (0110) bands of $^{12}\text{C}^{16}\text{O}_2$ and the (0002)_I - (0000) band of $^{13}\text{C}^{16}\text{O}^{18}\text{O}$.

¹B. Bezard, C. de Bergh, D. Crisp, and J.-P. Maillard, *Nature* **245**, 508 (1990).

²C. R. Pollock, F. R. Petersen, D. A. Jennings, and J. S. Wells, *J. Mol. Spectrosc.* **99**, 357 (1983).

Address of Giver and Chackerian: NASA AMES Research Center,
MS 245/4, Moffett Field, CA 94035-1000.

RF7 (2:57)

The ν_3 , $2\nu_2$ and ν_1 interacting bands of $^{14}\text{N}^{15}\text{O}_2$.

A. PERRIN*, A.M. VASSEROT*, C. CAMY-PEYRET*, J.M. FLAUD*, A. GOLDMAN** and
G. GUELACHVILI***.

Up to now, except for isolated states ^{1,2}, the spin-rotation interaction in NO₂ has been treated using a perturbation method ³. In the present work, an extensive analysis of NO₂ Fourier transform spectra in the 6.3 μm region has been performed leading to a large and precise set of spin-rotation levels of the (001), (020) and (100) interacting states of this molecule. Then, using an Hamiltonian which takes explicitly into account the Coriolis-type interaction between the levels of (001) and (020) and between those of (001) and (100) as well as the spin-rotation interaction, it has been possible to reproduce very satisfactorily the observed energy levels even in the case of strong resonances. Examples of the effects of such resonances will be given showing clearly that one needs to take them explicitly into account in order to reproduce within the experimental uncertainty the observed spectra.

¹A. Perrin, J.-M. Flaud, C. Camy-Peyret, B. Carli and M. Carlotti, *Molec. Phys.* **63**, 791 (1988)

²A. Perrin, C. Camy-Peyret, J.-M. Flaud and J. Kauppinen, *J. Mol. Spectrosc.* **130**, 168 (1988)

³W.T. Raynes, *J. Chem. Phys.* **41**, 3020 (1964)

Address : * LPMA, Bte 76, T13, CNRS and Université P. et M. Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France.

** Department of Physics, University of Denver, Denver, Colorado 80208-0202

*** LPMA, CNRS et Université Paris-Sud, Bât.350, 91405 Orsay Cedex, France.

Intermission

RF8 (3:20)

ABSOLUTE INTENSITY AND PRESSURE BROADENING MEASUREMENTS IN THE ν_2 FUNDAMENTAL OF N_2O J. W. JOHNS, M. NOEL AND T. L. TAN

Preliminary measurements of absolute intensities and self broadened line widths have been made in the ν_2 fundamental band of N_2O near 588 cm^{-1} . The linear Herman-Wallis factor is important in this band and a precise value has been obtained.

Some factors which affect intensity measurements made near the peak of the room temperature black body radiation curve will be discussed.

Address of Johns and Noel: Herzberg Institute of Astrophysics, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada K1A 0R6

Address of Tan: National University of Singapore, Department of Physics, Faculty of Science, Lower Kent Ridge Road, Singapore 0511

RF9 (3:32)

ABSOLUTE RAMAN INTENSITY MEASUREMENTS FOR HYDROGEN SULFIDE

W. F. MURPHY AND J. M. FERNÁNDEZ-SÁNCHEZ

Raman scattering cross sections have been measured for vibrational bands in the trace and anisotropy Raman scattering spectra of gaseous H_2S , and of several mixtures of D_2S , HDS , and H_2S . The analysis of this data in terms of the derivatives of the molecular polarizability derivatives with respect to symmetry coordinates permits the determination of the cross sections for the individual bands of the three isotopic species. These results can be used to predict the effect of vibration-rotation interaction on the intensities of lines in the pure rotational Raman spectrum of these molecules.

The current status of this work will be presented.

Address: Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Canada K1A 0R6

RF10 (3:49)

THE $2.5\text{ }\mu\text{m}$ BANDS OF OZONE: LINE POSITIONS AND INTENSITIES

A. PERRIN, A.-M. VASSEROT, J.-M. FLAUD, C. CAMY-PEYRET, V. MALATHY DEVI, M. A. H. SMITH, C. P. RINSLAND, A. BARBE, S. BOUAZZA, AND J. J. PLATEAUX

A study of high-resolution (0.010 cm^{-1}) Fourier transform absorption spectra of $^{16}\text{O}_3$ in the region around 4020 cm^{-1} has been performed. This study has resulted in the first extensive analysis of the $\nu_1+3\nu_3$ band of this molecule and the first observation of weaker lines from its $4\nu_3$ and $3\nu_1+\nu_2$ bands.

The rotational energy levels of the (103), (004), and (310) vibrational states of ozone have been satisfactorily reproduced using a Hamiltonian matrix which takes explicitly into account the classical Coriolis interaction of (103) \leftrightarrow (004) together with the unusual Coriolis-type (103) \leftrightarrow (310) and Fermi-type (310) \leftrightarrow (004) interactions. Under these conditions precise vibrational band centers and rotational and coupling constants were obtained. Also, over 130 line intensities were measured with an accuracy of 2-4%. Analysis of these intensities has allowed the determination of the $\nu_1+3\nu_3$ and $3\nu_1+\nu_2$ vibrational transition moment constants. Finally, a complete list of line positions, intensities, and lower-state energies was generated for the $\nu_1+3\nu_3$, $4\nu_3$, and $3\nu_1+\nu_2$ bands of $^{16}\text{O}_3$.

Address of Perrin, Vasserot, Flaud, and Camy-Peyret: Laboratoire de Physique Moléculaire et Atmosphérique, Université Pierre et Marie Curie et C.N.R.S., Tour 13, 4 Place Jussieu, 75252 Paris Cedex 05, France.

Address of V. Malathy Devi: Physics Department, The College of William and Mary, Williamsburg, Virginia 23185

Address of Smith and Rinsland: NASA Langley Research Center, Atmospheric Sciences Division, Mail Stop 401A, Hampton, Virginia 23665-5225.

Address of Barbe, Bouazza, and Plateaux: Laboratoire de Physique Moléculaire, U.A. CNRS 776, Université de Reims, BP 347, 51062 Reims Cedex, France.

RF11 (4:01)

THE ν_2 BANDS OF THE MONOSUBSTITUTED ^{17}O -SPECIES OF OZONE

A. PERRIN, C. CAMY-PEYRET, J.-M. FLAUD, C. P. RINSLAND, M. A. H. SMITH, AND V. MALATHY DEVI

Using 0.005-cm^{-1} resolution room temperature Fourier transform spectra of ^{17}O -enriched ozone samples, the first extensive analysis of the ν_2 bands of $^{16}\text{O}^{17}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{16}\text{O}^{17}\text{O}$ has been performed. First, using ground state combination differences derived from the infrared spectra together with the available microwave transitions, the ground state constants were refined. Then, the (010) rotational levels were fitted leading to precise constants for the upper states of both molecules. Finally, using appropriate expansions of the transformed transition moment operators, it has been possible to generate a comprehensive list of the line positions and intensities for the ν_2 bands of both isotopic species.

Address of Malathy Devi: Department of Physics, College of William and Mary, Williamsburg, Virginia, 23185.

Address of Perrin, Camy-Peyret, and Flaud: Laboratoire de Physique Moléculaire et Atmosphérique, Université Pierre et Marie Curie et C.N.R.S., Tour 13, 3^e étage, 4 place Jussieu, 75252 Paris Cedex 05, France.

Address of Rinsland and Smith: Atmospheric Sciences Division, NASA Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665-5225.

RF12 (4:13)

H.R. INFRARED SPECTRUM OF $^{18}\text{O}_3$: ANALYSIS OF THE TRIAD $2\nu_1$, $\nu_1+\nu_3$ and $2\nu_3$

A. BARBE, S. BOUAZZA, J.J. PLATEAUX, J.F. FLAUD and C. CAMY-PEYRET

High resolution spectra of $^{18}\text{O}_3$ in the $5\text{ }\mu\text{m}$ have never been recorded up to now. To derive intensities and positions of the lines of isotopic ozone a set of spectra have been obtained with the new F.T.S. built in Reims [1].

The spectra of 98 % $^{18}\text{O}_3$ introduced in the absorption cell of 31.2 cm long, at different pressures (9.4 Torr, 6 Torr, 4 Torr) have been performed in one hour, with a signal to noise ratio of 800, at resolution of 0.003 cm^{-1} corresponding to a 3 m path difference, using stepping mode. The observed experimental results are derived from least squares fits on line shape. The accuracy is $7 \cdot 10^{-5}\text{ cm}^{-1}$ for wavenumbers and 4 % for absolute intensities.

For the analysis we used Watson's type hamiltonian [2] with 22 constants for each vibrational state (200, 101 and 002) and 9 coupling constants for Coriolis and Darling-Dennison resonances between these states.

Finally, we give all the set parameters, a portion of listing with assignments observed and calculated wavenumbers and intensities, as well as standard deviation for ν and S.

[1] J.J. PLATEAUX, D. COURTOIS, A. DELAHAIGUE, A. BARBE and P. JOUVE
Rev. Phys. Appliquée 21, 239-244 (1986)

[2] C. CAMY-PEYRET, J.M. FLAUD, M.A. SMITH, C. P. RINSLAND, V.M. DEVI,
J.J. PLATEAUX and A. BARBE, J. Mol. Spectry 141, 134-144 (1990)

Address of Barbe, Bouazza and Plateaux : Université de Reims, URA 1434, UFR Sciences, 51062 REIMS Cédex, France

Address of Flaud and Camy-Peyret : Laboratoire de Physique Moléculaire et Atmosphérique, Université P.M. Curie et CNRS Tour 13, 4 Place Jussieu, 75252 Paris Cédex 05, France

RF13 (4:30)

The ν_4 band of Carbonyl fluoride.

J.M. FLAUD*, C. CAMY-PEYRET*, A. GOLDMAN**, C.P. RINSLAND***, R.D. BLATHER-WICK**, F.J. MURCRAY**

COF₂ which has been postulated to be an important intermediate in the decomposition of chlorofluorocarbons in the upper atmosphere has been observed in the stratosphere through the identification of absorption features of its ν_6 , ν_4 and ν_1 bands by the ATMOS experiment. In addition, recently the ν_6 and ν_4 bands have been observed at very high resolution (0.002 cm⁻¹) using a balloon borne FTS (Denver University group). Since in order to analyse the atmospheric spectra it is necessary to know precisely the spectral parameters of the molecule, we have undertaken, using 0.002 cm⁻¹ resolution laboratory spectra, an extensive analysis of the ν_4 band of COF₂. It proved not possible to reproduce correctly the observed wavenumbers considering the $\nu_4 = 1$ state as isolated and it was necessary to take into account the nearby state located about 4 cm⁻¹ below. In this way the line positions were reproduced within their experimental uncertainty allowing to determine accurate band centers and rotational and coupling constants. Comparisons between a calculated and the experimental spectrum will be presented showing the quality of the results.

Address :

* LPMA, Bte 76, T13, CNRS and Université P. et M. Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France.

** Physics Department, University of Denver, Denver, Colorado 80208-0202

*** Atmospheric Sciences Division, NASA Langley Research Center, Mail Stop 401A, Hampton, Virginia, 23665-5255

RF14 (4:42)

AN ANALYSIS OF THE FAR INFRARED SPECTRUM OF ACETONE

Y. G. Smeyers, M. L. Senent and D. C. Moule

The Far Infrared spectrum of acetone has been analyzed and assignments have been made for (CH₃)₂CO, (CD₃)₂CO and CH₃CD₃CO. The potential surface $V(\theta_1, \theta_2)$ for the θ_1 and θ_2 torsional displacements was mapped out by structurally relaxed 6-31G* MO calculations and fitted to a double fourier expansion in 7 terms. The torsional Hamiltonian matrix was symmetrized by the G_{xx} non rigid group into 16 boxes and was solved variationally. Intensities were obtained from the calculated electric dipole moments and were combined with the torsional frequencies to predict the spectrum. The simple pattern of bands was attributed to the $A_1 - A_2 / A_2 - A_1 / A_1 - A_2$ combinations, which are X directed out of the plane. The intensities in the Y direction were calculated to be of the same magnitude but were not observed because of their broader rotational contour.

Address of Smeyers and Senent: Instituto de Estructura de la Materia, Consejo Superior de Investigaciones, C. Serrano 119 - 28006, Madrid, Spain.

Address of Moule: Department of Chemistry, Brock University, St Catharines, Ont., L2S3A1.

RF15 (4:59)

INFRARED DIODE LASER AND FOURIER TRANSFORM SPECTROSCOPY OF A LOW PRESSURE PREMIXED GAS FLAME

K.L. MCNESBY and R.A. FIFER

A new low pressure premixed gas burner flame apparatus has been constructed in our laboratory. This new facility is used to investigate the combustion of premixed gases which have relevance to the study of the combustion of energetic materials of interest to the army.

The burner flame is probed in the infrared by a tunable diode laser and also by Fourier transform spectroscopy. Spatially resolved species profiles and temperatures are used as a check against theoretical models of a low pressure (20 torr) premixed methane / nitrous oxide flame. Principal species used for temperature estimation are NO and CO.

Address of McNesby and Fifer: U.S. Army Ballistic Research Laboratory, Attn: SLCBR-IB-I, Aberdeen Proving Ground, MD, 21005-5066

RG1 (1:30)

LOW ENERGY ELECTRON-SILANE SCATTERING USING THE COMPLEX KOHN METHOD AND POLARIZED ORBITALS

WEIGUO SUN, C. W. McCURDY, and B. H. LENGFIELD III

The electron scattering of silane is studied using the complex Kohn method with polarized trial wavefunctions at incident energies between 0.01 and 7.5 eV. The differential, and the integrated cross sections reported here are the first *ab initio* calculations on silane which include target response. The polarizability of the target is well represented by a small polarized subspace of the whole space of unoccupied orbitals.

The integrated cross sections reported here are in excellent agreement with experiment values especially in the Ramsauer-Townsend minimum region. Comparison between our differential cross sections (DCS) and those of experiment are very satisfactory above 4 eV. Both theoretical and experiment DCS showed an apparent d-wave character of the shape resonance at 3 eV.

This study shows the effectiveness of the complex Kohn method and the methods used to incorporate target response, and indicates that it is feasible to accurately study electron scattering from molecules as large or larger than silane with an *ab initio* procedure.

Address of Sun and McCurdy: Department of Chemistry, The Ohio State University, Columbus, OH 43210.

Address of Lengsfeld: Lawrence Livermore National Laboratory, P. O. Box 808, Livermore, CA 94550.

RG2 (1:47)

ELECTRONIC STRUCTURE OF HCCO RADICAL

KYUNGSUN KIM AND ISAIAH SHAVITT

Several electronic states of the HCCO radical have been studied by *ab initio* SCF, MCSCF, CI, and UMP2 calculations. Geometry optimizations have been carried out with a TZP basis set at the UMP2 level for the lower two states and at the SDCI level for the upper two states. Generally-contracted Dunning correlation-consistent pVDZ and pVTZ basis sets have been used for the accurate energy determination.

The two lowest states form a Renner-Teller pair, degenerate (${}^2\Pi$) at the linear geometry and split into a bent ${}^1{}^2A''$ ground state and a linear ${}^1{}^2\Pi$ excited state which becomes ${}^2A'$ upon bending. Davidson-corrected 56-reference SDCI with a Dunning generally-contracted [431/31] basis set gives an energy difference of 981 cm^{-1} for the lower Renner-Teller pair. Two higher states, ${}^2{}^2A'$ and ${}^2{}^2\Pi$, also form a Renner-Teller pair with a barrier to the linearity of 311 cm^{-1} . The same level of calculation places these states about 32316 cm^{-1} above the ground state minimum. The bonding is mostly $\text{H}-\dot{\text{C}}=\text{C}=\text{O}$ in the two lowest states, and is $\text{H}-\text{C}\equiv\text{C}-\dot{\text{O}}$ in the upper pair of states. The equilibrium geometries of the various states are given in the following table.

Equilibrium Geometries for Several States of HCCO^a

| parameter | ${}^1{}^2A''$ | ${}^1{}^2\Pi(A')$ | ${}^2{}^2A'$ | ${}^2{}^2\Pi(A'')$ |
|--------------------------------|---------------|-------------------|--------------|--------------------|
| $R_{\text{HC}} (\text{\AA})$ | 1.071 | 1.058 | 1.063 | 1.050 |
| R_{CC} | 1.314 | 1.269 | 1.256 | 1.246 |
| R_{CO} | 1.167 | 1.172 | 1.345 | 1.338 |
| $\theta_{\text{HCC}} (^\circ)$ | 128.2 | 180.0 | 150.8 | 180.0 |
| θ_{CCO} | 169.9 | 180.0 | 172.0 | 180.0 |

^aOptimized at the UMP2 and SDCI levels with a Dunning TZP segmented-contraction basis set. The bent structures are in *trans* conformation.

Address of Kim and Shavitt: Department of Chemistry, The Ohio State University, Columbus, OH 43210, U S A

RG3 (2:04)

AN AB INITIO METHODOLOGICAL STUDY OF THE STRUCTURES AND EXCITATION ENERGIES OF THE (n, π^*) STATES OF N_2H_2

KYUNGSUN KIM, ISAIAH SHAVITT, AND JANET E. DEL BENE

A number of *ab initio* approaches have been used to determine the equilibrium structures, energies, and harmonic vibrational frequencies of N_2H_2 in the ground state and in the excited singlet and triplet (n, π^*) states. The methods include restricted (RHF) and unrestricted (UHF) Hartree-Fock, multiconfigurational self-configurational self-consistent field (MCSCF), single-reference (SRCI) and multireference (MRCI) configuration interaction including all single and double excitations from the reference configurations, and second-order Møller-Plesset perturbation theory (MP2) using RHF and UHF orbitals for the ground and excited states, respectively. Unlike the singlet excited state, for which broken-symmetry solutions were found at the RHF level¹, no symmetry breaking was encountered for the triplet state. The ground state MP2 structure of N_2H_2 , which has C_{2h} symmetry, is in excellent agreement with the experimentally determined structure. The excited states are predicted to have nonplanar C_2 structures with dihedral angles ranging from 96 to 106° for the triplet state and from 105 to 121° for the singlet. Except for the SRCI singlet adiabatic excitation energy, the effect of configuration interaction is to increase the vertical and adiabatic excitation energies of both excited states relative to the RHF values in single-reference calculations, and to decrease these excitation energies relative to the MCSCF values in multireference calculations, bringing the single-reference and multireference values into better agreement with each other. The MRCI vertical excitation energies are 2.6 eV for the triplet and 3.6 eV for the singlet, while the corresponding 0-0 transition energies are 1.9 and 2.9 eV, respectively.

¹Janet E. Del Bene, Kyungsun Kim, and Isaiah Shavitt, *Can. J. Chem.*, in press (1991).

Address of Kim and Shavitt: Department of Chemistry, The Ohio State University, Columbus, OH 43210, U.S.A.
 Address of Del Bene: Department of Chemistry, Youngstown State University, Youngstown, OH 44555, U.S.A.

RG4 (2:21)

AN *ab initio* STUDY OF $n \rightarrow \pi^*$ TRANSITION ENERGIES IN HYDROGEN-BONDED COMPLEXES

J. E. Del Bene, E. A. Stahlberg, and I. Shavitt

Ab initio single- and multi-reference CISD correlation-energy calculations have been performed on the ground states and the lowest-energy singlet excited states of H_2CO , H_2CNH , *trans*-HNNH, and *trans*-(CHO)₂, and complexes of these molecules with HF, to investigate the effect of hydrogen bonding on $n \rightarrow \pi^*$ transition energies. The ground state geometries of all monomers and complexes were optimized at MP2/6-31+G(d,p), and vertical $n \rightarrow \pi^*$ transition energies were computed at these geometries. For H_2CO and H_2CNH , which contain only a single chromophore, the blue shift of the $n \rightarrow \pi^*$ transition energy in the complex is similar to the ground state hydrogen bond energy, suggesting that the hydrogen bond is broken or severely weakened in the excited state. In contrast, for *trans*-HNNH and *trans*-(CHO)₂, which have two chromophoric groups, the blue shift of the $n \rightarrow \pi^*$ band in the complex is significantly less than the ground-state hydrogen bond energy, suggesting that the hydrogen bond remains essentially intact in the excited state. In these complexes, the $n \rightarrow \pi^*$ excitation occurs primarily in the nonhydrogen-bonded chromophoric group.

Address of Del Bene: Department of Chemistry, Youngstown State University, Youngstown, Ohio, 44555
 Address of Stahlberg and Shavitt: Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210

RG5 (2:38)

AN *AB INITIO* STUDY OF THE SO₂ ELECTRONIC SPECTRA IN THE 3900—1750 Å REGION

R. J. Zellmer and I. Shavitt

Ab initio SCF, MCSCF, single- and multi-reference CISD calculations have been performed on the ground state (¹A₁) and the six lowest-energy excited states (^{1,3}B₁, ^{1,3}B₂, and ^{1,3}A₂). The geometries of all the states were optimized at the MCSCF level (employing a valence CAS space) using a Dunning DZP ((11,7,2/9,5,1)→[6,4,2/4,2,1]) basis set. The vertical excitation energies at the ¹A₁ experimental, SCF optimized, and MCSCF optimized geometries and the minimum-minimum (T_e) transitions at the experimental and MCSCF optimized geometries were determined. The vertical emission energies at the experimental and MCSCF optimized excited state geometries were also calculated. In addition, the C_{2v} minimum crossing points of the potential energy surfaces of the ³A₂ – ³B₁ and ¹A₂ – ¹B₁ pairs of states were determined. Finally, selected properties for all states at their respective experimental and MCSCF optimized geometries were also determined.

Address of Zellmer and Shavitt: Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210

RG6 (2:55)

TORSION-ROTATION PERTURBATIONS IN ELECTRONIC SPECTROSCOPY. THE S₁ ← S₀ SPECTRUM OF 2-METHYL-1-NAPHTHOL.¹

X.-Q. TAN AND D. W. PRATT

2-Methyl-1-naphthol (2M1HN) is an interesting molecule that exhibits motion along two low frequency coordinates, the torsional motion of the methyl group and rotational isomerism about the C-OH bond. Both motions are restricted by significant barriers; additionally, they couple to the overall rotational motion of the molecule and may also interact with each other. In this report, we describe the fully resolved S₁ ← S₀ electronic excitation spectrum of 2M1HN recorded in the collision-free environment of a molecular beam. The spectrum exhibits two electronic origins; these may be assigned to the *cis* and *trans* rotamers uniquely using deuterium substitution techniques similar to those employed for the parent 1-naphthol.² Further, the two O₀⁰ bands show significant torsion-rotation perturbations like the parent 2-methylnaphthalene.³ Analyses of these yields values of the hindering potentials V₃ that restrict the internal motion of the methyl group, in both electronic states of both rotamers. We find significantly higher V₃ values for CH₃-group rotation in *trans*-2M1HN, evidencing a steric contribution to the barriers of both electronic states of this rotamer.

¹Work supported by NSF.

²J. R. Johnson, K. D. Jordan, D. F. Plusquellic, and D. W. Pratt, J. Chem. Phys. 93, 2258 (1990).

³X.-Q. Tan, W. A. Majewski, D. F. Plusquellic, and D. W. Pratt, J. Chem. Phys., in press.

Address of Tan: Department of Physics, University of Pittsburgh, Pittsburgh, PA 15260.

Address of Pratt: Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

Intermission

RG7 (3:25)

AB INITIO AND MODEL STUDIES OF WEAKLY BONDED CLUSTERS OF CARBON MONOXIDE

C. A. Parish, C. E. Dykstra, J. D. Augspurger,

The molecular mechanics for clusters (MMC) model constructs interaction potentials from electrical properties and parameters associated with the individual interacting molecules. MMC parameters have now been developed for carbon monoxide, and we have carried out MMC calculations on the structures, stabilities and interconversion potentials of a number of CO-containing complexes. *Ab initio* calculations have also been carried out on CO---HF and OC---HF using a large, multiply polarized basis with incorporation of electron correlation effects at the coupled cluster level. These calculations show the potential curve of both complexes to be extremely flat near the equilibrium separation, a feature that seems to be properly described by the MMC model.

Address of Parish, Dykstra and Augspurger: Department of Chemistry, Indiana University-Purdue University, Indianapolis, Indiana, 46205

RG8 (3:42)

AB INITIO CALCULATIONS OF RHENIUM COMPLEXES USING RELATIVISTIC EFFECTIVE CORE POTENTIALS

J. P. Blaudeau, R. Ross, R. Pitzer, P. Mougenot and M. Benard

The complexes $\text{Cl}_2(\text{OH})_2\text{ReReCl}_2(\text{PH}_3)_2$ and $\text{Re}_2\text{Cl}_8^{-2}$ were studied. Atomic basis sets were optimized for rhenium, chlorine, oxygen, and phosphorus for use with Christiansen relativistic effective core potentials. Recently the COLUMBUS graphical unitary group approach multi-configuration self-consistent field (MCSCF) program was modified to incorporate these potentials. Hartree-Fock and MCSCF calculations for these complexes were performed on the ground state and several excited states. Spin-orbit splittings of these states were found using a double group spin-orbit configuration interaction (CI) program. The known quadruple rhenium-rhenium bond was investigated and, as previously shown, was not found at the Hartree-Fock level. A MCSCF calculation on the ground state of the complexes showed this quadruple bond. The criteria chosen for the description of the bonds were the molecular orbital and CI coefficients. The lowest excited state for these complexes was found to be a 3A_1 , δ - δ^* state with spin-orbit coupling of the order of 50 cm^{-1} . Two other important excited states, for which calculations are proceeding, are the δ - δ^* singlet state and a ligand-metal charge transfer state.

Address of Blaudeau, Ross, Pitzer: Department of Chemistry, The Ohio State University, 120 W. 18th Ave., Columbus, Ohio 43210

Address of Mougenot and Benard: Laboratoire de Chimie Quantique, E.R. 139 du CNRS, Institut Le Bel, Université Louis Pasteur, 4 rue Blaise Pascal, 67000 Strasbourg, France

RG9 (3:59)

COPPER CHLORIDE: SPIN-ORBIT CI POTENTIAL CURVES

Nora M. Wallace and Russell M. Pitzer

Ab initio potential energy curves for the ground and low-lying excited states of CuCl have been calculated using relativistic effective core potentials in a spin-orbit configuration interaction study. Potential maxima and avoided crossings have been found that appear to be similar to those found in a previous study of CuF. Most of these maxima and avoided crossings are caused by the interaction of initially lower-energy bonding ionic potential curves with repulsive, covalent potential curves while some are caused by spin-orbit interactions. The presence of potential maxima could allow metastable vibrational states.

Address: Department of Chemistry, The Ohio State University, Columbus, OH 43210

RG10 (4:16)**ELECTRONIC STRUCTURES OF $\text{Np}(\text{C}_8\text{H}_8)_2$ AND $\text{Pu}(\text{C}_8\text{H}_8)_2$**

Agnes H. H. Chang and Russell M. Pitzer

Department of Chemistry

The Ohio State University

120 West 18th Ave.

Columbus, OH 43210

RG11 (4:33)**SPIN-ORBIT CI STUDY OF VALENCE AND RYDBERG STATES OF LiBe**

M. M. MARINO, W. C. ERMLER, C. W. KERN, AND V. E. BONDYBEY

Ab initio spin-orbit full configuration interaction calculations in the context of relativistic effective core potentials are reported for the weakly bound metal dimer LiBe , a 3-valence-electron system. The effects of basis set on the energies of valence and Rydberg states of the cluster are discussed, as are the effects of truncation of the CI on the energy of the latter states. Results at the dissociative limit of 40 bohr are compared to the experimental atomic spectra.

Address for Marino and Kern: Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, OH 43210

Address for Ermler: Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, NJ 07030

Address for Bondybevy: Institute für Physikalische Chemie der T. U. München, 8046 Garching, Germany and Department of Chemistry, The Ohio State University

RG12 (4:50)**AB INITIO SPIN-ORBIT CONFIGURATION INTERACTION CALCULATIONS ON THE Li_2Be CLUSTER**

M. AKBULUT, W. C. ERMLER

Relativistic ab initio spin-orbit configuration interaction calculations are carried out in order to investigate the electronic structure and geometry of the Li_2Be metal atom cluster. The calculations take into account both electron correlation and spin-orbit effects. The procedure for the treatment of spin-orbit coupling in molecules is based on the use of relativistic effective potentials derived from Dirac-Fock atomic wavefunctions. Double-group symmetry is used to define the molecular electronic states.

The ground state of Li_2Be has a linear symmetrical geometry having bond lengths of 2.5 Å. Several low-lying excited states are investigated and potential energy surfaces of the system are presented.

Address of Akbulut: Department of Physics, Stevens Institute of Technology, Hoboken, N.J., 07030, U.S.A.

Address of Ermler: Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, N.J., 07030, U.S.A.

FA1 (8:30)

ROTATIONAL SPECTRUM, STRUCTURE, AND DIPOLE MOMENT OF THE $\text{SiF}_4\text{-NH}_3$ SYMMETRIC TOP

R. S. RUOFF, T. EMILSSON, A. I. JAMAN, T. C. GERMANN, AND H. S. GUTOWSKY

It has been suggested recently that Si-F bonds are highly ionic in character,¹ and theoretical electron density analysis supports a strongly ionic Si-H bond in, for example, SiH_4 .² Microwave spectroscopy can address to some extent the nature of the Si-F and Si-H bonds. High quality ab initio calculations indicate a strongly bound axial dimer $\text{SiF}_4\text{-NH}_3$ with a calculated well depth of 10.5 kcal and a short Si-N bond distance.³ We have obtained the rotational spectra of various isotopically substituted $\text{SiF}_4\text{-NH}_3$ dimers (as well as of $\text{SiH}_4\text{-NH}_3$) and assigned them as symmetric tops with internal rotation present. For the main isotopic species of $\text{SiF}_4\text{-NH}_3$ we find $B_0 = 2502.4777$ MHz.

Analysis of the structure indicates that the $F_{ax}\text{-Si-}F_{eq}$ angle is about 97° differing greatly from the tetrahedral 109.5° . This change in geometry should give a large dipole moment for the dimer if the Si-F bond dipoles are large, as one would expect for an ionic bond. Ab initio calculations indicate a dimer dipole moment of 4.2 D,⁴ which exceeds the sum of monomer moments by 2.7 D. We plan to report the dipole moment, compare the experimentally derived geometry with the ab initio calculated geometry, and discuss the internal rotation of the SiF_4 and NH_3 tops.

Spectra were observed with a Balle/Flygare pulsed nozzle, Fourier transform spectrometer. Assignment of the internal rotation states was aided by observing a time profile of the population of the state as the gas pulse evolves, with the internal rotor state populations remarkably dependent on whether the front, middle, or end of each gas pulse is probed. This effect will also be discussed.

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Address of Ruoff: T. J. Watson Research Center, IBM, Yorktown Heights, NY 10598.

Address of Emilsson, Jaman, Germann, and Gutowsky: Noyes Chemical Laboratory, University of Illinois, Urbana, IL 61801

FA2 (8:47)

MICROWAVE ROTATIONAL SPECTRUM AND ELECTRICAL PROPERTIES OF Kr-BENZENE

T D KLOTS, T. EMILSSON, AND H. S. GUTOWSKY

We have recently observed the microwave rotational spectrum for several isotopic versions of the Kr-benzene (Bzn) dimer, including that of Kr-82, 83, 84 and 86. In agreement with an earlier, rotationally resolved UV study of the analogous Ar-Bzn dimer,¹ and ongoing work on Kr-Bzn,² the complex is confirmed as having C_{6v} symmetry. The ground state rotational constants determined for the ^{84}Kr -Bzn dimer are $B_0 = 795.6822$ MHz, $D_J = 1.315$ kHz, and $D_{JK} = 7.90$ kHz. The B_0 translates into a Kr to Bzn center of mass distance of 3.675 Å.

In addition, we have been interested in the electrical properties of the complex and have measured the (induced) ^{83}Kr nuclear quadrupole coupling constant, $\chi_{aa} = -5.021$ MHz, as well as the purely induced electric dipole moment, $\mu_a = 0.136$ D. These experimentally observed induced parameters are more closely reproduced by a calculated benzene charge distribution³ employed in a distributed multipole analysis than in a central multipole model.

¹Th. Weber, A. von Barga, E. Riedle, and H. J. Neusser, J. Chem. Phys. **92**, 90 (1990).

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Address of Klotz: Chemistry Division, Argonne National Laboratory, Argonne, IL 60439.

Address of Emilsson and Gutowsky: Noyes Chemical Laboratory, University of Illinois, Urbana, IL 61801.

FA3 (9:04)

K \neq 0 TRANSITIONS IN THE ROTATIONAL SPECTRUM OF Ar-HCN

T. C. GERMANN, T. EMILSSON, AND H. S. GUTOWSKY

The Ar-HCN dimer has been described¹ as "a highly nonrigid molecule," with several spectroscopic anomalies attributed to strong angular-radial coupling in the interaction potential.¹⁻⁴ In earlier work only K = 0 transitions were observed and the dimer has been viewed as pseudolinear. However, a previously calculated potential surface² exhibits a local *maximum* for the linear structure and a minimum for structures bent by $\sim 15^\circ$, with smaller angles favored at larger Ar to HCN separations.

We now report the observation of four very weak K \neq 0 transitions which suggest that the Ar-HCN ground state structure is indeed bent, with (B-C) = 16 MHz. The line centers are given below, in MHz. Those for K = 0 are from earlier work.^{1,2}

| $J \rightarrow J'$ | K = -1 | K = 0 | K = +1 |
|--------------------|---------|---------|---------|
| 1 \rightarrow 2 | 6418.00 | 6433.89 | 6448.84 |
| 2 \rightarrow 3 | 9615. | 9640.87 | 9664. |

Analysis of the hyperfine structure of the K \neq 0 transitions, produced by quadrupole interactions of the ¹⁴N, gives coupling constants which are quite different from those determined for the K = 0 transitions. Further analysis is in progress and will be discussed.

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³G. T. Fraser and A. S. Pine, J. Chem. Phys. **91**, 3319 (1989); R. E. Bumgarner and G. A. Blake, Chem. Phys. Lett. **161**, 308 (1989).

⁴D. C. Clary, C. E. Dateo, and T. Stoecklin, J. Chem. Phys. **93**, 7666 (1990).

Address: Noyes Chemical Laboratory, University of Illinois, Urbana, IL 61801.

FA4

MICROWAVE SPECTRUM OF NaBH₄

Y. KAWASHIMA, C. YAMADA, AND E. HIROTA

FA4 and FA5 have been
rescheduled at end of
Session WH

The rotational spectrum of NaBH₄ was observed in the millimeter-wave region using a high temperature absorption cell. The observed spectrum of NaBH₄ showed the pattern of a symmetric top molecule: strong and weak for K=3n and 3n \pm 1, respectively, because of the nuclear spin statistical weight for C_{3v} symmetry. The rotational and centrifugal distortion constants for the ¹¹B and ¹⁰B species were determined. The observed rotational constants of Na¹¹BH₄ and Na¹⁰BH₄, combined with the assumption that r(B-H_b) - r(B-H_t) = 0.04 Å and $\theta(\text{H}_b\text{-B-H}_t) = 111^\circ$, gave estimates for r(Na-B) and r(B-H) to be 2.308 \pm 0.006 Å and 1.28 \pm 0.10 Å, respectively. This bond length obtained for Na-B is much shorter than the reported value in crystal; 3.08 Å. The bond lengths derived indicate that NaBH₄ has a tridentate molecular structure with three bridging hydrogens. This result agrees with those of ab initio calculations. In addition, two other sets of the rotational spectra were observed; one had a larger centrifugal distortion constant D_{JK} than that of the ground state, while the other a negative centrifugal distortion constant D_{JK}, and the k structures of both the spectra were irregular at k=0, 1, and 2. These spectra are assigned to the excited vibrational states of NaBH₄.

Address of Kawashima: Kanagawa Institute of Technology, 1030 Shimo-ogino, Atsugi, Kanagawa 243-02, Japan

Address of Yamada and Hirota: Institute for Molecular Science, Okazaki, 444, Japan.

FA5

MICROWAVE SPECTRUM OF LiBH_4

Y. KAWASHIMA AND E. HIROTA

The rotational spectrum of LiBH_4 was observed in the millimeter-wave region using a high temperature absorption cell. The observed spectrum of LiBH_4 showed the pattern of a symmetric top molecule as in the case of NaBH_4 : strong and weak for $K=3n$ and $3n+1$, respectively. The rotational and centrifugal distortion constants for the $^7\text{Li}^{11}\text{BH}_4$, $^7\text{Li}^{10}\text{BH}_4$, and $^6\text{Li}^{11}\text{BH}_4$ species were determined. Three observed rotational constants of LiBH_4 gave the r_g bond distance between the boron and lithium atoms to be 1.9394 Å. This bond length obtained for Li-B is much shorter than the reported value in crystal; 2.47 Å. The bond lengths derived indicate that LiBH_4 has a tridentate molecular structure with three bridging hydrogen atoms. Furthermore, assuming that $\angle(\text{H}_b\text{-B-H}_t) = 113^\circ$, two bond distances $r(\text{B-H}_b)$ and $r(\text{B-H}_t)$ were obtained to be 1.256 and 1.216 Å, respectively. This result agrees with those of ab initio calculations.

Address of Kawashima: Kanagawa Institute of Technology, 1030 Shimo-ogino, Atsugi, Kanagawa 243-02, Japan

Address of Hirota: Institute for Molecular Science, Okazaki, 444, Japan and the Graduate University for Advanced Studies, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan.

FA6 (9:50)

THE ARGON-FORMIC ACID VAN DER WAALS COMPLEX

I. I. IOANNOU, K. W. HILLIG II, AND R. L. KUCZKOWSKI

Seventeen a- and b-dipole transitions of the $\text{Ar}\cdot\text{HCOOH}$ van der Waals complex have been observed by Fourier Transform microwave spectroscopy. They were fit with a Watson A-reduced Hamiltonian to rotational constants $A = 12116.629(3)$ MHz, $B = 1663.523(1)$ MHz, $C = 1459.382(1)$ MHz. The dipole moment of the complex was determined as 1.305(1) D. Along with the normal species, seven b-type lines for both the ^{13}C and DCOOH species were measured, in order to obtain the structure. The rotational constants indicate that the complex is planar. The two subunits are separated by a distance $R_{cm} = 3.73(1)$ Å. The argon lies on the hydroxyl side, with the next closest heavy atom being the carbonyl oxygen.

Address: Department of Chemistry, University of Michigan, 930 N. University Ave., Ann Arbor, Michigan 48109, U.S.A.

FA7 (10:15)

DIPOLE MOMENTS OF THE OCS-NE, OCS-AR AND OCS-KR VAN DER WAALS COMPLEXES L. NEMES, S. L. MARUCA, A. M. ANDREWS, K. W. HILLIG II, AND R. L. KUCZKOWSKI

Values of the electric dipole moment for the van der Waals complexes of carbonyl sulfide with krypton, argon and neon were determined from Stark-effect measurements in a cavity Fourier-transform microwave spectrometer. The dipole moment components are: Ne-OCS, $|\mu_a| = 0.3294(11)$ D, $|\mu_b| = 0.6224(35)$ D; Ar-OCS, $|\mu_a| = 0.2094(10)$ D, $|\mu_b| = 0.6573(23)$ D; Kr-OCS, $|\mu_a| = 0.1719(18)$ D and $|\mu_b| = 0.6746(10)$ D.

The observed values were interpreted using *ab initio* theoretical calculations of the induced dipole moment of the rare gas component in the complex. In addition, some simple analytical models -- based on the expansion of the OCS multipole moments -- were also tested to rationalize the observed dipole moments. An attempt to assess the extent of zero-point vibrational effects in the harmonic oscillator limit will also be reported.

Address of Andrews, Maruca, Hillig and Kuczkowski: Department of Chemistry, University of Michigan, 930 N. University Ave., Ann Arbor, Michigan 48109, U.S.A.

Address of Nemes: Research Laboratory for Inorganic Chemistry, Hungarian Academy of Sciences, Budaörsi út 45, POB 132, H-1502 Budapest, Hungary.

FA8 (10:27)

THE ν_4 FUNDAMENTAL BANDS OF TRANS AND CIS-HNO₂.

L. KLEINER, J. M. GUILMOT, M. CARLEER AND M. HERMAN

The ν_4 fundamental band of both the trans and the cis isomers of HNO₂ ranges in an infrared atmospheric window. The previous spectroscopic investigations reported in the literature (1-3), although accurate, present however limitations either in the range scanned or in the spectral resolution and intensity. We have refined the analysis on the basis of improved experimental conditions, both of instrumental and chemical natures. Some 1950 lines of a-type are now assigned to the ν_4 fundamental band of trans-HNO₂ and over 3100 lines of a and b-type to the ν_4 fundamental band of cis-HNO₂. The results will be presented and relative intensity information will be discussed.

1. C. M. Deeley and I. M. Mills, J. Mol. Struct., **100**, 199-213 (1983).

2. A. G. Maki and R. L. Sams, J. Mol. Struct., **100**, 215-221 (1983).

3. C. M. Deeley, I. M. Mills, L. O. Halonen and J. Puuppinen, Can. J. Phys., **63**, 962-966 (1985).

Address of Kleiner: Molecular Physics Division, National Institute for Standards and Technology, Gaithersburg, MD 20899, USA

Address of Guilmot, Carleer and Herman: Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles, CP160, 50, av. F-D Roosevelt, 1050 Bruxelles, Belgium.

Intermission

FA9 (11:39)

MICROWAVE SPECTRUM AND STRUCTURE OF $\text{CH}_3\text{CN-BF}_3$

M.A. Dvorak, R.S. Ford, F.J. Lovas, R.D. Suenram and K.R. Leopold

The gas phase adduct $\text{CH}_3\text{CN-BF}_3$ has been observed by rotational spectroscopy. The structure is that of a symmetric top with the nitrogen end of the CH_3CN toward the boron. The B-N bond length is 2.010 ± 0.020 Å and the NBF angle is $95.3^\circ \pm 1.4^\circ$. The structure is reminiscent of the classical dative bond chemistry known for adducts of BF_3 with nitrogen containing donors, and of related weakly bound complexes of BF_3 , but is extremely unusual in that the bond length and the NBF angle are intermediate between the limits normally observed for van der Waals or covalently bonded systems. Moreover, the B-N bond length is 0.4 Å longer than that determined in the solid state by X-ray crystallography, indicating a significant influence of neighboring molecules in the crystal on the structure of a single dimeric unit. We draw analogy with well known crystallographic work of Dunitz and coworkers, and interpret the structure as a snapshot along the reaction path for the formation of the boron - nitrogen dative bond.

Address of Dvorak and Leopold: Department of Chemistry, University of Minnesota, Minneapolis, MN 55455

Address of Ford: University of Minnesota, Morris, Morris, MN 56267

Address of Lovas and Suenram: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

FA10 (10:56)

MICROWAVE CHARACTERIZATION OF POLY-PARA-PHENYLENE-BENZOBIS-THIAZOLE (PBT). J. Campbell, H. Hejase and P. K. Kadaba U. of Kentucky, Lexington, Ky; and K. Naishadam, Wright State University, Dayton, Ohio.

Film samples of the polymer poly-para-phenylene-benzobis-thiazole (PBT) are implanted at room temperature with multiple implants of I and Kr ions up to total fluences of 10^{16} and 10^{17} ions/cm². Ion energies and corresponding doses are determined using an analytical version of the TRIM code to achieve a uniform implant distribution to a depth of approximately 0.1 µm. The microwave conductivity of the implanted samples is measured using a microwave network analyzer and a cavity-perturbation technique. The latter eliminates the need to evaluate the depolarization factor which has a large uncertainty for arbitrarily shaped samples. A prototype design of a millimeter wave (FET) will be discussed. Results have been analyzed in terms of an energy-dependent hopping model.

Address of Campbell, Hejase and Kadaba: University of Kentucky, Department of Electrical Engineering, Lexington, Ky.

Address of Naishadam: Wright State University, Department of Electrical Engineering, Dayton, Ohio.

FA11 (11:08)

THE MICROWAVE SPECTRUM OF CYCLOPENTADIENYL-COBALT-DICARBONYL

S.G.Kukolich, M.A. Roehrig, Qi-Qi Chen, R.E. Bumgarner and S.T. Haubrich

Rotational transitions in the 6 - 18 GHz range were measured for the organometallic complex cyclopentadienyl-cobalt-dicarbonyl. The spectrum was obtained using a Flygare-Balle type pulsed beam spectrometer. A series of $\Delta J = 1$ and some $\Delta J = 0$ transitions were obtained for this π -dipole hindered rotor. Splittings of rotational lines due to ^{59}Co quadrupole and hindered rotation effects were observed. The spectrum was analysed using a "free rotor" basis set. Preliminary analysis indicates an intermediate barrier with V_0 on the order of 1 THz.

Address of Kukolich, Roehrig, Chen, and Haubrich : Department of Chemistry, The University of Arizona, Tucson, Arizona, 85721

Address of Bumgarner: Division of Geological and Planetary Sciences 170-25, California Institute of Technology, Pasadena, Ca. 91125

FA12 (11:20)

MICROWAVE MEASUREMENTS OF COBALT AND NITROGEN QUADRUPOLE COUPLING IN $\text{Co}(\text{CO})_3\text{NO}$

M.A.Roehrig, S.G. Kukolich, S.T. Haubrich, and J.A. Shea

$J = 2 \rightarrow 3$, $3 \rightarrow 4$, $4 \rightarrow 5$ and $5 \rightarrow 6$ transitions in the oblate symmetric top molecule cobalt tricarbonyl nitrosyl were measured using a Flygare-Balle type pulsed beam microwave spectrometer. $K = 0$ and $K = 3$ transitions were observed for $J = 3 \rightarrow 4$ and $4 \rightarrow 5$. Hyperfine structure due to ^{59}Co and ^{14}N nuclear quadrupole coupling interactions was well resolved. The measured quadrupole coupling strengths are $eQq_{cc}(^{59}\text{Co}) = 35.14(29) \text{ MHz}$ and $eQq_{cc}(^{14}\text{N}) = -1.59(10) \text{ MHz}$. Measured rotation and distortion constants are $B_0 = 1042.1590(4) \text{ MHz}$ and $D_J = 0.17(8) \text{ kHz}$. The measured B value is 4% smaller than the B value calculated from electron diffraction data. Spin-rotation and a quadrupole distortion term were also obtained for ^{59}Co .

Address of Kukolich, Roehrig, Haubrich, and Shea : Department of Chemistry, The University of Arizona, Tucson, Arizona, 85721

FA13 (11:32)

DETERMINATION OF THE STRUCTURES OF THE CONFORMATIONS OF DIPROPYL ETHER. KIMBERLEY J. GRANT, A.R. HIGHT, STEWART E. NOVICK, AND ROBERT K. BOHN

Microwave spectroscopy of dipropyl ether has been performed by supersonic jet molecular beam electric resonance spectroscopy, by conventional waveguide-cell techniques, and by molecular beam pulsed-jet Fourier Transform spectroscopy (for which we are indebted to Professor R.L. Kuczkowski for machine time). It appears that there are several distinct conformations present in dipropyl ether even at the low temperatures achieved by supersonic expansion. The geometries of these conformations will be discussed.

Address of Grant, Hight, and Novick: Department of Chemistry, Wesleyan University, Middletown, CT 06459

Address of Bohn: Department of Chemistry, University of Connecticut, Storrs, CT 06269-3060

FB1 (8:30)

SUGGESTED GROUND STATE FREQUENCY AND BOND ENERGY FOR NiF T. C. DEVORE, M. MCQUAID, J. L. GOLE

The reaction between nickel atoms and molecular fluorine produces a chemiluminescent flame arising primarily from the NiF molecule. A partial vibrational analysis for four band systems of NiF indicated that the ground state vibrational frequency of $\sim 625 \text{ cm}^{-1}$, not 740 cm^{-1} as reported previously. An energy analysis of the high energy emission features indicated that the dissociation energy of NiF is $4.4 \pm .2 \text{ eV}$.

Address of DeVore: Department of Chemistry, James Madison University, Harrisonburg, VA 22807.

Address of McQuaid and Gole: School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332.

FB2 (8:47)

LASER SPECTROSCOPY OF VIBRATIONALLY-EXCITED RYDBERG STATES OF H_3^+

L. J. LEMBO, H. HELM, AND D. L. HUESTIS

In an earlier study¹ we observed the $3p \ ^2E'(v_1=0, v_2=1)$ and $3p \ ^2E'(v_1=1, v_2=1)$ states of H_3^+ in vibronically-allowed excitation from the metastable $N = 0 \ ^1\tilde{B} \ 2p \ ^2A_2'$ state. In the present work we use these $3p$ states as intermediate levels in two-color excitation of autoionizing vibrationally-excited Rydberg series.

Rydberg states with principal quantum numbers from $n = 6$ to $n = 50$ are observed. The strongest transitions correspond to nd Rydberg series converging to the $N^+ = 1$ and $N^+ = 2$ states, with $G = 0$, of vibrationally excited H_3^+ . Weaker transitions are observed to nd Rydberg states converging to $N^+ = 3$ and $N^+ = 4$ levels, also with $G = 0$. There is also evidence for excitation of np (or nf) Rydberg states built upon $G = 3$, $N^+ = 2$ and $N^+ = 3$ cores.

An MQDT analysis is currently in progress.

*Research supported by AFOSR and NSF

¹L. J. Lembo, H. Helm, and D. L. Huestis, J. Chem. Phys. **90**, 5299 (1989).

Address of Helm and Huestis: Molecular Physics Laboratory, SRI International, Menlo Park, CA 94025

Current address of Lembo: TRW, 1 Space Park, Redondo Beach, CA 90278

FB3 (9:04)

INFRARED LASER SPECTROSCOPY OF THE C_2H RADICAL

W-B. YAN AND T. AMANO

A $2\Pi - 2\Sigma$ band of gas phase C_2H centered at 2928 cm^{-1} is observed using a high resolution difference-frequency laser spectrometer. The C_2H molecules were produced in a hollow cathode discharge in a mixture of C_2H_2 ($\sim 15 \text{ mTorr}$), H_2 ($\sim 0\text{-}150 \text{ mTorr}$), and He ($\sim 700 \text{ mTorr}$). Measurements were carried out using discharge modulation method at 3 kHz with a current of about 800 mA . Total laser pathlength was 36 m in a White cell arrangement. We have tentatively assigned this band to be the $3\nu_2 + \nu_3$ combination band of C_2H . In addition, two $2\Pi - 2\Pi$ transitions of C_2H connecting known states were also recorded. The common lower level of the two bands is the $\tilde{X} (0 \ 1 \ 0)$ state, with the upper levels being the same as those of the known 3693 and 3600 cm^{-1} bands, respectively.

Address Herzberg Institute of Astrophysics, National Research Council, Ottawa, Canada K1A 0R6

FB4 (9:21)

STIMULATED EMISSION PUMPING SPECTROSCOPY OF JET COOLED NCO

F. J. NORTHRUP, TREVOR J. SEARS AND MING WU

Stimulated emission pumping has been used to measure vibration-rotation levels in the ground electronic state of NCO at energies of up to 6500 cm^{-1} . The radicals were formed in the reaction of $\text{CN} + \text{O}_2$ in the throat of a supersonic free jet expansion of a mixture of cyanogen and oxygen in nitrogen carrier gas. The expansion mixture was excited by an excimer laser at 193 nm immediately after the nozzle orifice causing the cyanogen to dissociate. The reaction and subsequent cooling of the NCO product radicals occurs as the expansion proceeds and the radicals were probed in the collision free region of the expansion some 12-15 mm from the nozzle. Many of the rovibronic levels probed have never before been observed and will provide interesting tests of approximate treatments of the combined effects of Renner-Teller and spin-orbit coupling and Fermi-resonance interactions in the radical. We have made a systematic study of the $(v_1, v_2, v_3) = (00v_3)$ levels up to $v_3 = 3$ and many examples of $(v_1, v_2, 0)$ and $(v_1, v_2, 1)$ Fermi-resonant multiplets with both Π and Σ vibronic symmetries.

Address of Northrup Sears and Wu: Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973.

FB5 (9:38)

INFRARED FLASH KINETIC SPECTROSCOPY OF THE KETENYL RADICAL

KENNETH G. UNFRIED, GRAHAM P. GLASS AND R. F. CURL

The high resolution infrared spectrum of the heavy atom antisymmetric stretch vibration of the ketenyl radical (HCCO) has been observed by means of infrared kinetic spectroscopy using 193 nm photolysis of ketene followed by diode laser probing of the transient absorption. Individual ro-vibrational transitions have been identified near the band origin located at approximately 2023 cm^{-1} . This spectroscopic technique will be presented, along with the observed spectra, assignments and parameters obtained from a least squares fit of the data.

Address: Chemistry Department Rice University, Houston TX 77251

FB6 (9:55)

INFRARED DIODE LASER ABSORPTION SPECTROSCOPY OF HOCO

WAFAA M. FAWZY AND TREVOR J. SEARS

We have detected the infrared spectrum of the HOCO radical in the C=O stretching region around 1850 cm^{-1} . The radical was formed by excimer laser photolysis of acetic acid (CH_3COOH) or acrylic acid ($\text{C}_2\text{H}_3\text{COOH}$) at 193 nm and its infrared spectrum measured by diode laser absorption spectroscopy. The observed spectrum has the structure expected for a parallel, α -dipole, band as would be predicted based on the expected radical structure and by comparison with the analogous band of isoelectronic FCO. P, Q and R branch lines have been detected and the band origin lies slightly above 1850 cm^{-1} which compares with the 1843 cm^{-1} reported¹ for the band in a low temperature argon matrix. The detailed assignment of the K_a rotational structure in the spectrum is currently in progress and results will be reported at the meeting. When the spectrum is assigned, it should prove to be an ideal vehicle for measurement of chemical reaction rates on a state by state basis.

¹ M. E. Jacox, J. Chem Phys **88**, 4598-4607 (1988)

Address of Fawzy and Sears: Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973.

FB7 (10:12)

DIRECT ABSORPTION SPECTROSCOPY OF CARBON CLUSTERS IN THE VISIBLE REGION

F. SCAPPINI, W.-B. YAN, AND T. AMANO

Direct absorption spectroscopy with a dye laser as a radiation source has been employed to detect electronic transitions of carbon clusters. To enhance the sensitivity, concentration modulation technique in a cooled hollow cathode discharge is used. The technique has proved to be a sensitive method for detection of ions and free radicals in the infrared region with a difference-frequency laser as a radiation source. As the noise sources of the difference-frequency laser are the Ar^+ and dye lasers, similar sensitivity is expected to be attained in visible absorption spectroscopy with a dye laser. In this investigation, absorption spectra were recorded in the $16900 - 17100 \text{ cm}^{-1}$ region in a hollow cathode discharge in a mixture of C_2H_2 and He. The same lines were also observed in the discharge of C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8 , and C_2D_6 . As the fully deuterated ethane yielded the same spectra, we conclude the carrier (or carriers) of the spectra contains no hydrogen.

Address of Scappini: Istituto di Spettroscopia Molecolare del CNR, 40126 Bologna, Italy.

Address of Yan and Amano: Herzberg Institute of Astrophysics, National Research Council, Ottawa, Canada K1A 0R6

Intermission

FB8 (10:40)

STARK SPECTROSCOPY OF $^{13}\text{CD}_3\text{OH}$ AND CH_3OD WITH THE HCN LASER.

G.R. SUDHAKARAN, R.M. LEES, R.L. BHATTACHARJEE, AND I. MUKHOPADHYAY

Laser Stark Spectra of $^{13}\text{CD}_3\text{OH}$ and CH_3OD were investigated at the $\lambda = 311 \mu\text{m}$ and $337 \mu\text{m}$ lines of the HCN laser. The spectra were taken for both parallel and perpendicular polarizations at Stark electric fields up to 60000 V/cm . For $^{13}\text{CD}_3\text{OH}$, the extensive series of absorption lines observed at $311 \mu\text{m}$ were assigned to the $J = 8$ to 12 members of the $K = 2 \leftarrow 3$ E_1 Q branch in the $\nu_1 = 1$ torsional state. One of the resonances observed at $337 \mu\text{m}$ was tentatively identified as the $J_k = 18_2 \leftarrow 17_1 A^-$, $\nu_1 = 0$ transition.

For CH_3OD , numerous families of resonances were observed at both of the laser lines. The Q branch transition observed at $311 \mu\text{m}$ was assigned as $J_k = 18_1 \leftarrow 18_0 E_2$, $\nu_1 = 1$ torsional state. Zero field frequencies for all the assigned transitions are given with improved accuracy over those calculated from available molecular constants.

Address of Sudhakaran: Department of Physics, SUNY at Oswego, Oswego, NY 13126

Address of Lees: Department of Physics, University of New Brunswick, Fredericton, New Brunswick, Canada E3B5A3

Address of Bhattacharjee: Department of Chemistry, University of Rochester, Rochester, NY 14627

Address of Mukhopadhyay: Center for Advanced Technology, Rajendranagar, Indore 452012, India

FB9 (10:57)

THE JET-COOLED FLUORESCENCE EXCITATION SPECTRUM AND RING-BENDING POTENTIAL ENERGY FUNCTION AND CONFORMATION OF 2-CYCLOPENTEN-1-ONE IN THE $S_1(n,\pi^*)$ ELECTRONIC EXCITED STATE

C. M. CHEATHAM AND JAAN LAANE

The jet-cooled fluorescence excitation spectra of 2-cyclopenten-1-one and its 5,5- d_2 isotopomer have been recorded in the 370 to 340 nm region. The electronic origin for the unrelaxed species occurs at 27210 cm^{-1} for the $S_1(n,\pi^*)$ electronic excited state. The vibrational frequencies for the three carbonyl motions and the nine ring modes were observed for the excited state. Bands at 67, 158, and 256 cm^{-1} for the d_0 species, at 63, 147, and 240 cm^{-1} for the 5- d_1 isotopomer, and at 59, 138, and 227 cm^{-1} for the d_2 species were assigned to the ring-puckering motion in the S_1 state. A single one-dimensional potential energy function accurately fit the data for all three isotopomers. This function is nearly purely quartic in character and shows the ring to be planar in the electronic excited state. However, it has become less rigid, and this is ascribed to a decrease in initial angle strain within the ring. The C=O and C=C stretching frequencies occur at 1418 and 1357 cm^{-1} for the d_0 molecule. The ring-twisting frequency for the S_1 state occurs at 274 cm^{-1} . Previous electronic absorption measurements had resulted in a misassignment for this motion. The vibrational data for the electronic excited state will be compared to ground state values recently obtained by far-infrared spectroscopy.¹

¹C. M. Cheatham and J. Laane, *J. Chem. Phys.*, **94**, in press (April), (1991).

Address of authors: Department of Chemistry, Texas A&M University, College Station, TX 77843

FB10 (11:14)

DESIGN AND OPERATION OF A SUPERSONIC JET AND LASER-INDUCED FLUORESCENCE EXCITATION APPARATUS FOR ANALYSIS OF VIBRATIONAL LEVELS IN ELECTRONIC EXCITED STATES

M. CHEATHAM, J. ZHANG, M. HUANG, N. MEINANDER, M. B. KELLY, P. SAGEAR, and J. LAANE

An experimental apparatus, based on a Nd:YAG laser system, for fluorescence excitation spectroscopy in a supersonic jet has been constructed and optimized for the collection of spectra from weakly fluorescing samples. The critical experimental parameters and the methods necessary for their determination will be discussed. Details relating to experimental timing, optical alignment, supersonic jet operation, and nozzle design are of special importance. A detailed description of the hardware and software will be presented.

The spectra obtained at low temperatures for various carbonyl compounds, such as 2-cyclopenten-1-one, 1-propanal, and 1-propynal, will be shown. These can be analyzed to determine the vibrational levels and molecular conformations in the electronic excited states.

Address: Department of Chemistry, Texas A&M University, College Station, TX 77843

FB11 (11:31)

LASER-INDUCED FLUORESCENCE SPECTROSCOPY OF THE INERT GAS - MOLECULAR RADICAL VAN DER WAALS COMPLEXES $X\text{-CdCH}_3$ ($X = \text{He, Ne, Ar, Kr, and Xe}$)

Andrew M. Ellis, Eric S. J. Robles, and Terry A. Miller

During a recent spectroscopic study of CdCH_3 , in which this radical was prepared in a free jet expansion by laser photolysis of $\text{Cd}(\text{CH}_3)_2$, weak bands were found to be present adjacent to CdCH_3 vibronic features which were attributed to clusters of the type $X\text{-CdCH}_3$ where X represents an inert gas atom.¹ We have successfully recorded laser excitation spectra for the cases where $X = \text{He, Ne, Ar, Kr, Xe}$. The $\Lambda\text{-}\Lambda$ electronic origins of these clusters have been determined and all are found to be blue-shifted with respect to the $\Lambda\text{-}\Lambda$ 0_0^0 band of CdCH_3 . Furthermore, vibrational structure has been resolved in the spectra of He-CdCH_3 , Ne-CdCH_3 , Ar-CdCH_3 , and Kr-CdCH_3 . We will discuss this vibrational structure and will also present preliminary results from a study of the $\text{H}_2\text{-CdCH}_3$ cluster.

¹ E. S. J. Robles, A. M. Ellis, and T. A. Miller, *Chem. Phys. Lett.*, accepted for publication

Address of authors: The Laser Spectroscopy Facility, The Ohio State University, 120 W 18th Ave., Columbus, OH 43210

FB12 (11:48)

HIGH RESOLUTION SPECTROSCOPY OF BENZYL AND RELATED RADICALS

Tai-Yuan David Lin, Timothy M. Cerny, James M. Williamson, and Terry A. Miller

Rotationally resolved LIF electronic spectra of jet cooled benzyl radical have been recorded for the type-A A^1 and type-B $6a_0^1$ bands. Calibrated band frequencies, ground state and excited state rotational constants have been well determined. Results confirm and extend earlier contour analysis of spectra obtained with absorption techniques.¹ Recent results from other aryl-substituted radicals will also be presented.

¹ C. Cossart-Magos and W. Goetz, *J. of Mol. Spec.* **115**, 366 (1986).

Address of Lin, Cerny, Williamson, and Miller: The Ohio State University, Laser Spectroscopy Facility, Department of Chemistry, 120 West 18th Avenue, Columbus, Ohio 43210.

FB13 (12:00)

Determination of Vibronic Degeneracy Lifting and Jahn-Teller Distortion in Asymmetrically Deuterated Cyclopentadienyl Radicals by High Resolution Laser Spectroscopy

Lian Yu, David W. Cullin, James M. Williamson and Terry A. Miller

The lifting of vibronic degeneracy in cyclopentadienyl radical upon asymmetric deuteration has been studied using high resolution laser spectroscopy. Both the magnitude of the splitting and the ordering of the symmetric and antisymmetric components were determined. The splittings in $\text{C}_5\text{H}_4\text{D}$ and C_5HD_4 were found to have similar magnitude (about 9 cm^{-1}) but opposite ordering. Depending on the orbital symmetry, the structure of the split levels undergoes substantial elongation or compression from the regular pentagon structure. The degree of distortion was precisely measured and related to the Jahn-Teller effect in the molecule.

Address of Authors: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 West 18th Avenue, Columbus, Ohio 43210

FB14 (12:17)**Rotationally Resolved Laser Induced Fluorescence Spectroscopy of Free Radical-Inert Gas Complexes: $C_5H_5...He$, $C_5H_5...He_2$, $C_5H_5...Ne$ and $CH_3-C_5H_4...He_2$**

Lian Yu, James M. Williamson, David W. Cullin and Terry A. Miller

We have recorded rotationally resolved laser induced fluorescence spectra of free radical-inert gas complexes in a supersonic free jet expansion. From the rotational analysis, we were able to determine the location of inert gas atoms in the complexes. In general, the inert gas atoms are found to bind to the center of the aromatic rings. The separation from the ring typically undergoes a substantial decrease upon electronic excitation. The electronic orbital movement and methyl torsion in the complexes are compared with uncomplexed molecules.

Address of Authors: Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 West 18th Avenue, Columbus, Ohio 43210

FC1 (8:30)

A VAN DER WAALS COMPLEX STUDY OF THE ORIENTATION DEPENDENCE IN COLLISIONAL RELAXATION OF GLYOXAL(S_1) BY Ar

Luc Lapierre and Hai-Lung Dai

Van der Waals forces can be used to control the orientation of two molecules in a collisional process. In the collision induced intersystem crossing process



each isomer of the Glyoxal-Ar complex corresponds to a different region for the collisional interaction to occur. Also, excitation of the van der Waals vibrational levels of the complex allows fine control of the collisional energy as well as the direction. The glyoxal molecule in the complex is excited to the S_1 state. In the laser induced fluorescence following the S_1 excitation, a bi-exponential decay corresponding to successive irreversible decays of the initial excitation was observed: intersystem crossing of glyoxal(S_1)-Ar (first exponential) followed by vibrational predissociation of Gl(T_1)-Ar (second exponential). The results show that Ar interacting with the oxygen orbital gives an intersystem crossing rate two orders of magnitude faster than the interaction with the π^* orbital.

Address: Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323

FC2 (8:47)

A COMPARISON OF EXPERIMENTAL AND *AB INITIO* CROSS SECTIONS FOR ROTATIONALLY AND VIBRATIONALLY INELASTIC SCATTERING FROM S_1 GLYOXAL IN COLLISIONS WITH He.

K.W. Butz, H. Du, B.D. Gilbert, D. Krajnovich and C.S. Parmenter.

Crossed molecular beams have been used to study rotationally and vibrationally inelastic scattering from several vibrational-rotational initial levels of 1A_g (S_1) glyoxal in collisions with He. The cross sections obtained in our spectroscopic experiments can now be compared to those predicted by *ab initio* calculations [Kroes, Rettschnick and Clary, Chem. Phys. 148, 359 (1990)]. The predictions show that substantial differences exist between the cross sections for rotationally inelastic scattering from the 0^0 and 7^2 initial levels. The calculations also show that there are differences between the rotationally inelastic scattering cross sections from the 0^0 level for scattering by H_2 and He. The emerging experimental data for inelastic scattering of glyoxal with He shows the same trends. The experimental cross sections for excitation (or de-excitation) are larger for scattering from 7^2 than for 0^0 and the rotationally inelastic cross sections for scattering from 0^0 depend on whether H_2 or He are used as the collision partners.

Address of Gilbert and Parmenter Department of Chemistry, Indiana University, Bloomington, IN 47405

Address of Butz Department of Chemistry, School of Science, Griffith University, Nathan QLD 4111 Australia

Address of Du Bldg. 200, Rm. K121, Chemistry Division, Argonne National Laboratory, 9700 S. Cass Ave. Argonne, IL 60439

Address of Krajnovich IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120

FC3 (9:04)

PHOTOLYSIS OF CH₃COOD IN THE FIRST ¹(n,n*) BAND

D. R. PETERMAN AND J. A. GUEST

Following near-uv excitation of gas-phase acetic acid-d, nascent OD photofragments have been probed using laser fluorescence excitation. The partially deuterated parent species was chosen to examine the effect of moving the fragment center-of-mass away from oxygen, relative to the OH center-of-mass. Results will be compared to OH internal state distributions measured following photolysis¹ of CH₃COOH, to assess the dynamical changes resulting from isotope substitution.

¹S. S. Hunnicutt, L. D. Waits, and J. A. Guest, *J. Phys. Chem.* **95**, 562 (1991); **93**, 5188 (1989).

Address: Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172

FC4 (9:16)

EFFECT OF CLUSTERING ON ELECTRONIC RADIATIONLESS DECAY: THE SUPPRESSION OF "CHANNEL THREE" IN BENZENE COMPLEXES

M. Y. Hahn, P. Y. Cheng, S. S. Ju, and Hai-Lung Dai

"Channel Three" refers to the intramolecular mechanism responsible for the sudden and anomalous fluorescence quenching at about 3,000 cm⁻¹ above the origin of the benzene S₁ state. Previous studies¹ found high rotational selectivity in Channel Three, suggesting that Channel Three is promoted by rotation induced vibrational mixing.

This hypothesis is born out in the study of the fluorescence decay in benzene/acetylene complexes. Dramatic increase in fluorescence lifetimes and yields, in comparison with the benzene molecule, in the Channel Three region was observed in certain structural isomers of the benzene/acetylene complexes in which the molecular rotation of benzene along its top axis is hindered by intermolecular interactions.

¹E. Riedle, H. J. Neusser and E. W. Schlag, *Phil. Trans. R. Soc. Lond.* **A332**, 189 (1990), and references therein.

Address: Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323

FC5 (9:33)

METHYL ROTOR ACCELERATION OF VAN DER WAALS BOND DISSOCIATION A SPECTROSCOPIC VIEW.

Z. Q. Zhao and C. S. Parmenter

The molecules p-difluorobenzene (pDFB) and p-fluorotoluene (pFT) differ by the presence of a nearly free methyl rotor in the latter. It is well established by spectroscopy that the methyl rotor has a big effect on the intramolecular dynamics of these molecules, with two orders of magnitude methyl rotor acceleration of intramolecular vibrational energy redistribution (IVR). We have now begun to study the dissociation of the van der Waals complexes with argon. We find a similar acceleration of dissociation. The S₁-S₀ fluorescence spectra of pFT-Ar and pDFB-Ar complexes differ qualitatively. The dissociation rate is so accelerated in pFT-Ar that emission from the undissociated S₁ complex can no longer be observed. Without quantitative constraints, we can account for the increased dissociation rates by the proposition that the methyl rotor boosts the rate of IVR inside the complex itself.

Address of Zhao and Parmenter Department of Chemistry, Indiana University Bloomington, IN 47405

FC6 (9:50)**Time resolved Measurements of State resolved Collisional Energy Transfer in the Electronic Ground State of NH₃ with IR-Double(Triple)-Resonance Spectroscopy****B. Abel, S.L. Coy, J.J. Klaassen, and J.I. Steinfeld**

The energy transfer of vibrationally and rotationally excited states of polyatomic molecules is of fundamental interest for molecular spectroscopy and for the kinetics of many reactive systems. In the present contribution, state resolved measurements of collisional energy transfer in NH₃ in the $v_2=1$ and $v_2=2$ regions are presented.

The v_2 levels of NH₃ have been populated by CO₂ laser excitation: one photon in the $v_2=1$ region and two photon (identical and non-identical) in the $v_2=2$ region. With this technique, selected well defined states in the regions of $v_2=1$ and 2 have been prepared. The detection of changes in population of these and other neighboring states has been monitored by transient IR absorption spectroscopy with a diode laser. Line widths in the $3v_2-2v_2$ bands have provided some information about energy transfer in the $3v_2$ region. Measurements of total depopulation rates of selected states (e.g. $k(v_2=1, s(5,3)) = 30\mu s^{-1} \text{ torr}^{-1}$), rates of collision induced symmetry change ($a \rightarrow s$), and individual $k_{ij}(\Delta J=1)$ between different states in the energy regions v_2 and $2v_2$ are found to be faster than the Lennard-Jones rate ($10\mu s^{-1} \text{ torr}^{-1}$), which is in accord with theoretical expectations. The experiments show that vibrational energy loss is much slower than rotational energy transfer

A detailed master equation analysis and direct state-resolved measurements provide "state to state" rate constants and their vibrational energy / inversion splitting dependence for NH₃-NH₃ rotational energy transfer. Preliminary work on foreign gas broadening will be described.

Address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass. 02139

Intermission**FC7 (10:20)****TRANSLATIONAL ENERGY STUDY OF CH₃ PHOTOFRAGMENTS RESULTING FROM 266-NM EXCITATION OF ACETONE****L. D. WAITS, R. J. HORWITZ, AND J. A. GUEST**

Excitation of a molecular beam of acetone at 266 nm leads to methyl photofragments that have been examined by resonant multiphoton ionization/time-of-flight mass spectrometry. Analysis of the arrival time profile of CH₃⁺ reveals a broad translational energy distribution for vibrationless methyl photofragments. The mean translational energy corresponds to 39% of the energy available following dissociation to CH₃CO + CH₃. The mean photofragment recoil energy for a two-body dissociation will be compared to the acetone dissociation barrier height, and discussed in the context of related experiments on the α -cleavage dynamics of acetic acid performed in this laboratory. Preliminary studies of the near-uv photo-chemistry of related ketones will also be presented.

Address: Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172

FC8 (10:37)

VIBRATIONAL RELAXATION OF OZONE IN O₃-O₂ AND O₃-N₂ GAS MIXTURES FROM INFRARED DOUBLE-RESONANCE MEASUREMENTS

F. MENARD, L. DOYENNETTE, J. MENARD and J.M. FLAUD

Numerous close coincidences can be found between CO₂ laser lines and O₃ rovibrational lines assigned to different fundamental and hot bands such as ν_1 , ν_3 , $\nu_1 + \nu_3 - \nu_1$, $2\nu_3 - \nu_3$, $\nu_2 + \nu_3 - \nu_2$, ... Therefore it proved possible to study collision-induced vibrational energy transfers in O₃ by means of a time-resolved double-resonance technique using two CO₂ lasers.

These experiments performed in the neat gas as well as in mixtures with O₂ and N₂ have allowed to observe a very fast intermode transfer occurring between the ν_1 and ν_3 Coriolis-coupled modes and to measure the corresponding rate constant. The near-resonant vibrational energy transfer populating the $\nu_2 + \nu_3$ state has also been investigated, as well as the $(\nu_1, \nu_3) \rightarrow \nu_2$ intermode transfer and the vibrational deexcitation of the ν_1 , ν_2 and ν_3 states.

From a simplified analytical treatment of the kinetic model we have deduced the rate coefficients corresponding to the investigated processes.

Address : LPMA, Bte 76, T13, CNRS and Université P. et M. Curie, 4, Place Jussieu, 75252 Paris Cedex 05, France.

FC9 (11:49)

INFRARED SPECTROSCOPY OF HIGHLY VIBRATIONALLY EXCITED HOOH, HONO₂, AND (CH₃)₃COOH

P. R. Fleming, M. Li, and T. R. Rizzo

The infrared absorption of molecules subsequent to vibrational overtone excitation reveals the presence (or absence) of vibrational state mixing at the excited level and provides information about the nature of the dark states that mix with the zeroth-order bright state. We have used an optical-infrared double resonance method to measure the infrared spectrum of the vibrationally excited HOOH, HONO₂, and (CH₃)₃COOH. A pulsed dye laser first excites a 4 \leftarrow 0 OH stretch overtone transition. An infrared pulse from a Nd:YAG pumped optical parametric oscillator then excites the molecule to a state above its dissociation threshold. The infrared spectrum is generated by monitoring the OH predissociation product via laser induced fluorescence as the infrared frequency is scanned.

The 4 ν_{OH} level of HOOH is at most only very slightly mixed, and this fact allows us to perform sequential local mode-local mode double resonance excitation of the two equivalent OH oscillators. In contrast, the 4 ν_{OH} level of HONO₂ and (CH₃)₃COOH are extensively mixed. In these two molecules, the zeroth-order dark states appear to mix with the bright state in proportion to their relative density at the 4 ν_{OH} energy, regardless of their vibrational character.

This work has been supported by the Department of Energy, Office of Basic Energy Sciences

Address of Authors: Department of Chemistry, University of Rochester, Rochester, NY 14627

FC10 (11:06)

INFRARED-OPTICAL DOUBLE RESONANCE SPECTROSCOPY OF THE (4, 1) LOCAL-LOCAL OH STRETCH COMBINATION BAND OF HOOH

X. Luo and T. R. Rizzo

We have investigated the (4, 1) local-local OH stretch combination band of hydrogen peroxide using infrared-optical double resonance. A pulse from a Nd:YAG pumped optical parametric oscillator excites an OH stretch fundamental of HOOH and selects a single or small subset of rotational states. A dye laser pulse then promotes the molecules above the threshold for O-O bond dissociation by a $4\leftarrow 0$ vibrational overtone excitation of the other OH stretch. The overtone absorption is detected by monitoring the OH dissociation fragment *via* laser induced fluorescence. The rotationally resolved vibrational overtone spectra generated by this technique indicate that the band origin of the $4\leftarrow 0$ OH stretch transition in an HOOH molecule containing one quantum of OH stretch in the other oscillator is shifted by -13.2 cm^{-1} from the direct $4\leftarrow 0$ transition of the ground state molecule.¹

These spectra also provide the opportunity to prepare reactant molecules in single rovibrational states at energies close to the dissociation threshold. The OH product state distributions resulting from the decomposition of these selectively excited molecules reveals the presence of a small barrier in the exit channel of the potential energy surface. The overtone excitation spectra indicate that the top of the barrier lies at $17,054\text{ cm}^{-1} \pm 5\text{ cm}^{-1}$, and the OH product state distributions set a lower limit of 190 cm^{-1} for the barrier height.

¹C. Douketis and J. P. Reilly, J. Chem. Phys. 91, 5239 (1989).

This work has been supported by the U.S. Department of Energy, Office of Basic Energy Sciences.

Address of authors: Department of Chemistry, University of Rochester, Rochester NY 14627

FC11 (11:23)

CONTRASTING EIGENSTATE BEHAVIOR IN THE METHYL STRETCH REGIONS OF 1-BUTYNE AND ETHANOL: EVIDENCE FOR CORIOLIS AND/OR CENTRIFUGAL IVR MECHANISMS IN ETHANOL

G. A. BETHARDY, J. GO, D. S. PERRY

Sub-Doppler infrared absorption spectra of 1-butyne and trans ethanol cooled in a slit jet expansion under the same conditions are reported. Spectra of the c-type component of the asymmetric methyl C-H stretch near 2990 cm^{-1} exhibit a substantially different appearance in these molecules. Mixing of the zero-order methyl C-H stretch vibration with bath vibrational (or rotational-vibrational) states gives rise to multiplets of molecular eigenstates. This behavior is the spectroscopic signature of the kinetic phenomena of intramolecular vibrational redistribution (IVR). Such eigenstates are assigned unambiguously to zero-order transitions by comparison of ground state combination differences to microwave data for $J' = 0-4$ and $Ka' = 0-2$.

Both molecules reveal fragmentation of each upper state rotational level into multiplet of molecular eigenstates. However, in ethanol a dramatic increase in the number of coupled levels as a function of J' indicates the presence of a Coriolis or centrifugal coupling mechanism for IVR. This is in sharp contrast to 1-butyne where no such strong rotational effect is observed suggesting a primarily anharmonic mechanism. The data provide a test of the keyhole model which was previously proposed to explain IVR in these molecules. According to the model the bright state (C-H stretch) and the primary anharmonic coupling to the bath is similar in each case. However, the couplings among the zero-order bath states is different for the two molecules. The asymmetric internal O-H rotor in the ethanol molecule allows for rotationally induced coupling mechanisms among vibrational bath states and for exploration of much of the available rotational-vibrational phase space. In contrast, no rotational effects are found in 1-butyne and the anharmonic bath couplings allow for exploration of vibrational phase space only.

Address: Department of Chemistry, University of Akron, Akron, Ohio, 44325.

FC12 (11:40)

Energy transfer properties of the lowest excited electronic state of CO:

$a^3\Pi_J$, G.A. Rogaski, J.M. Price, A.M. Wodtke,

Because of the strong UV emission of the CO metastable $a^3\Pi_J$ in the Martian atmosphere, much effort has been invested in the study of the collisional quenching processes of this state of CO. In addition, it is believed that the cross-section for collisional intersystem crossing is near gas kinetic so this molecule offers itself as a convenient arena for experimental investigations of the collisional dynamics of intersystem crossing. Despite the large amount of effort, no state specific studies of the collisional dynamics have been performed.

In this experiment a tunable Argon fluoride laser was used to state selectively prepare individual rotational, vibrational, spin-orbit and lambda doublet quantum states of the $a^3\Pi_J$ state of Carbon monoxide. This was accomplished using direct excitation in the Cameron system ($a^3\Pi_J \leftarrow X^1\Sigma^+$). Detection of the prepared as well as collisionally populated states was achieved with laser induced fluorescence of the Herman bands ($e^3\Sigma^- \leftarrow a^3\Pi_J$). This provides a sensitive means of studying the state specific collision dynamics. Results of these studies will be reported. In addition, double resonance spectroscopy of the strongly perturbed $e^3\Sigma^-$ states which interact with $A^1\Pi$ will be presented.

Address of Authors: Department of Chemistry, University of California, Santa Barbara, California, 93106

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 RE4, FA6, FA7
 KUKOLICH, S. G.--FA11, FA12, WE10
 KULCKE, A.--ME3
 KUMBHARKHANE, A. C.--RE11

L

LAANE, JAAN--MF11, TC2, TC3, TC4,
 FB9, FB10
 LACOME, N.--WF1
 LAFFERTY, WALTER J.--RA11, RF2
 LANGHOFF, S. R.--TC1
 LANGLOIS, S.--WF12
 LAPIERRE, LUC--PC1
 LARSEN, L.--TF4
 LAUSH, C.--ME3
 LEE, S.--TE13
 LEE, S. S.--TA6, TA7
 LEES, R. M.--PB8
 LEGON, A. C.--TF'8
 LEHMANN, K. K.--WF13, RB11, RC1,
 RC2, RC3, RC4, RC5, RC7
 LEIBOWITZ, S. J.--TC2, TC3
 LEMBO, L. J.--PB2
 LENGSPIELD, B. H., III--RG1
 LEOPOLD, K. R.--TB2, WH9, FA9
 LE ROY, R. J.--MG9, TE3, TE4,
 TE5, TE6
 LESPADDE, L.--TC5, WG9
 LEWIS-BEVAN, W.--TF'1, TF'2, TF'3
 LEWERENZ, MARIUS--TB1
 LIMBACH, P. A.--WE6
 LIN, P.--WH8
 LIN, TAI-YUAN DAVID--PB12
 LIN, Y.--ME5
 LIN, Y. Q.--WH8
 LIN, Z.--RC12
 LINNARTZ, H.--ME8
 LINTON, C.--TB11, TB13
 LISY, J. M.--ME3
 LITTLE, T. S.--TC6
 LOETE, M.--TA3
 LONGHI, G.--TC5, WG9
 LOONEY, J. P.--WF2
 LOVAS, P. J.--ME6, TE8, TE9, TE10,
 TE11, RE7, RE8, FA9
 LOVEJOY, R. W.--RF1
 LUCCHESSE, R. R.--TF'7, TF'8

LUCIA, J. P.--RC9, RC10
 LUNDBERG, J. K.--RB1
 LUO, X.--PC10

M

MAGUIRE, W. C.--MF12
 MAJEWSKI, W. A.--TA12
 MALATHY DEVI, V.--WF4, WF5, WF7,
 WF10, WF11, RF10, RF11,
 Presiding over session TA
 MALON, PETR--WG5, WG6
 MANDIN, J.-Y.--WF3
 MANTZ, A. W.--RF3, Presiding
 over session TF and TF'
 MANZANARES, CARLOS--TC13
 MARINO, M. M.--RG11
 MARNEY, K.--RB9
 MARSHALL, A. G.--WE6
 MARSHALL, M. D.--ME12, ME13,
 Presiding over session ME
 MARTIN, F.--TB11
 MARTIN, P. A.--TB6
 MARUCCA, S. L.--FA7
 MASON, M. A.--RC7
 MATHEWS, C. W.--MF1, Presiding
 over session FB
 MATSUMURA, K.--TE11
 MAYRHOFER, R. C.--TC8
 MCCARTHY, P.--RB9
 MCCORMICK, RODNEY--Presiding over
 session WH
 MCCOY, A. B.--TC7, TC9
 MCCURDY, C. W.--RG1
 MCDERMOTT, M. T.--TC14, WE6
 MCILROY, A.--RC3
 MCKELLAR, A.R.W.--MF8, RA3, RA4,
 TA12
 MCNESEBY, K. L.--RF15
 MCPHERSON, G.--RB9
 MCQUAID, M.--PB1
 MEERTS, W. L.--ME8
 MEHROTRA, S. C.--RB11
 MEIER, V. A.--TC14
 MEINANDER, N.--FB10
 MELENDEZ, F. J.--RA7
 MENARD, F.--FC8
 MENARD, J.--FC8
 MENTEL, T. F.--RC4, RC5, RC6
 MERDES, D. W.--MF13
 MERER, A. J.--TB1
 MICKELSON, M. B.--TF4
 MICKLEY, LORETTA J.--WG5
 MILLER, R. E.--ME12, ME13
 MILLER, S.--TA7

MILLER, T. A.--TG7, TG11, TG12,
 RB2, RB3, RB4, RB5, FB11, FB12
 FB13, FB14
 MOAZZEN-AHMADI, N.--MF8
 MOMOSE, TAKAMASA---RB8
 MOUGENOT, P.--RG8
 MOULE, D. C.--RB7, RF14
 MUENTER, J. S.--ME1, ME2, ME13,
 Presiding over session ME
 MUKHOPADHYAY, I.--PB8
 MUMMA, M. J.--WF1
 MURCRAY, F. J.--RF13
 MURPHY, W. F.--RP9

N

NAFIE, L. A.--WG1, WG2, WG3, WG4
 NAISHADAM, K.--FA10
 NASH, JOHN--WH6
 NELSON, D. D., JR.--ME8
 NELSON, H. H.--WH3
 NEMES, L.--FA7
 NESBITT, D. J.--RC3
 NIIDE, YUZURU--RB9
 NINO, A.--RB7
 NOEL, M.--RF8
 NORTHROP, F. J.--PB4
 NOVICK, STEWART B.--PA13

O

OGATA, TERUHIKO--RB9
 OHASHI, N.--TB7
 OKA, T.--TA6, TA7, TA8, TA9,
 TA10, TA11, TF1, TF2, TF3
 OKUNISHI, M.--RC8
 ORMSBY, P. S.--TA2
 ORTIGOSO, J.--RA11
 OZIER, I.--MF8, WH7

P

PAGE, T. W.--RE10
 PARISH, C. A.--RG7
 PARKINSON, W. H.--TB7, TB8
 PARMENTER, C. S.--RB6, FC2, FC5
 PASTERNAK, LOUISE--WH3
 PATE, B. H.--RC3, RC4, RC5, RC6
 PAWELKE, G.--WF9
 PEARSON, ANN--TC1
 PEARSON, J. C.--RE2
 PERRIN, A.--RP7, RF10, RF11
 PERRY, D. S.--PC11
 PETERMAN, D. R.--FC3
 PICKARD, S. T.--WG7
 PICKETT, H. M.--MA1, TA4

PINE, A. S.--ME7, MF13, WF2, RA8,
RA9, RA10
PIOCOS, ELIZABETH A.--MG6
PITZER, R. M.--WE3, RG8, RG9, RG10
PLATEAUX, J. J.--RF10, RF12
PLIVA, J.--MF13
POLAVARAPU, P. L.--WG7, WG8, WG11,
Presiding over session WG
PRASAD, C.V.V.--TB12
PRATT, D. W.--TG4, RG6
PRESILLA-MARQUEZ, J. D.--MG11
PRICE, J. M.--FC12
PURANIK, S. M.--RB11
PURSELL, C. J.--TA9

Q

QUINONES, A.--TF'7

R

RAGUNATHAN, N.--WG2, WG4
RAKOWSKY, S.--TG10
RAM, R. S.--TB3
RAO, K. NARAHARI--TA2, TB6, TF4
REDDY, S. PADDI--TB12, TF5
REEVE, S. W.--TB2, WH9
REHPUSS, B.--TG7, TG11
REILLY, JAMES P.--RC9, RC10, RC11,
RC12
REUTER, D. C.--WF14
RICE, J. K.--WH3, Presiding over
session TG
RICHARDSON, HUGH--WG13
RINSLAND, C. P.--WF4, WF5, WF7,
WF10, WF11, RF10, RF11, RF13
RITBY, C.M.L.--MG11
RIVERA-GAINES, V. E.--TC2
RIZZO, T. R.--FC9, RC10
ROBLES, ERIC S. J.--RB2, RB3, RB4,
RB5, PB11
ROPERIG, M. A.--PA11, PA12
ROGASKI, C. A.--FC12
ROMANINI, D.--WF13
ROSENMANN, L.--WF12
ROSS, A. J.--TB11
ROSS, R.--RG8
ROSSLEIN, M.--TA6, TA8, TA10
ROTHMAN, L. S.--WF3, Presiding
over session WF
RUOFF, R. S.--FA1

S

SADOVSKII, D.--TA12, TB5
SAGEAR, P.--PB10

SAITO, S.--TG8
SALVADORI, P.--WG9
SANDERS, J.--WH7
SAYKALLY, R. J.--WH1, WH2
SCAPPINI, F.--FB7
SCHAEFER, J.--RA4
SCHWEIKHARD, L. C.--WE6
SCHWENDEMAN, R. H.--MF4, MF5, MF6,
Presiding over session MF
SCOLES, G.--RC3, RC4, RC5, RC6
SCUSERIA, GUSTAVO E.--WE9
SEARS, T.--RF4, FB4, FB6
SEIBERT, G.--WF9
SEMENT, M.L.--RF14
SEVERANCE, DANIEL L.--WH4
SHAVITT, ISIAH--RG2, RG3, RG4,
RG5
SHEA, J. A.--PA12
SHEN, L. N.--MG10, WE7
SHIN, U.--MF6
SIBET, E. L., III--TC7, TC8, TC9
SILBEY, R. J.--RA6
SIMARD, B.--TB13
SINISTA, L. N.--TA1
SIROTA, J. M.--WF14
SJAATUD, D. D.--RB10
SLANGER, T. G.--TG3
SLEE, TOM--TB4, TE5
SLOTTERBACK, T. J.--TG4
SLUIS, KATHLEEN--WG5, WG6
SMYERS, Y. G.--RB7, RF14
SMITH, H. E.--WG7
SMITH, M.A.H.--WF4, WF5, WF7,
WF10, WF11, RF10, RF11
SMITH, PETER L.--TB7
SNAVELY, D. L.--Presiding over
session RC
SONG, Q.--MF4, MF5
SONG, X.--RC9, RC10
SPANO, F.--RC2
SPENCER, M. N.--WF8
STAHLBERG, E. A.--RG4
STARK, G.--TB7
STARRS, C.--TG9
STEINFELD, J. I.--FC6
STEPHENS, P. J.--TF'4, TF'5,
TF'6
STEVERT, DAVID W.--WH1, WH2
STOCKMAN, P. A.--ME9
STONE, STEPHEN C.--RF2
STORK, W. D.--TF'1, TF'3
STROH, F.--MF3
STWALLEY, W. C.--TG1
SUCKLEY, A.--TF'8
SUDHAKARAN, G. R.--FB8, Presiding
over session RB

SUENRAM, R. D.--ME6, ME7, TE8,
TE9, TE10, TE11, WH1, RE5, RE7,
RE8, FA9
SUH, M. H.--TG7
SUN, L. H.--ME1
SUN, WEIGUO--RG1
SUNI, I.--TE13
SUTTER, D. H.--MA3
SUZUKI, S.--ME9
SWIFT, PAUL--TE1
SZAFRANSKI, M.--ME2

T

TAINÉ, J.--WF12
TALEB-BENDIAB, A.--ME10, ME11
TAM, S.--TB3
TAN, T. L.--RF8
TAN, X.-Q.--RG6
TARRAGO, G.--WF1
TELLINGHUISEN, J.--MB4, TG5
TENNYSON, J.--TA7
THOMAS, MICHAEL--TC11, TC12
THOMPSON, WARREN E.--MG4
THORNE, A. P.--TB8
TODD, F. G.--RB6
TRAPTON, L. M.--WA5
TRETYAKOV, M. YU--RE5
TRUDEL, M.--WG10
TSAI, B. P.--RB13
TSENG, SHAO-HUI--TB1
TSUCHIYA, S.--RC8

U

UANG, J.-Y.--WG5, WG6
UNFRIED, KENNETH G.--FB5
URBAN, S.--RA1

V

VALDERAMA, G. L.--TG1
VAN ZEE, R. J.--MG12, MG13
VASSEROT, A. M.--RF7, RF10
VENTRUDO, B. P.--TA7
VERGES, J.--TB11
VERVLOET, M.--TA12, TB5
VILLA, M.--RA7
VILLARREAL, J. R.--TC3

W

WAITS, L. D.--FC7
WALLACE, N. M.--RG9
WANG, B.--RA2
WANG, Z.--TF'8, RC13

WATSON, J.K.G.--WA5
 WATTS, ROBERT O.--TB1
 WATTSON, R. B.--WF6
 WEBER, M.--MF12
 WELTNER, W., JR.--MG12, MG13
 WESTERN, C. M.--TG4
 WILLIAMSON, J. M.--TG11, FB12,
 FB13, FB14
 WINNEWISSER, B. P.--MF2, WF9,
 TA2
 WINNEWISSER, M.--MF2, MF3, WF9,
 TA2
 WITHEY, F. A.--WE7
 WODTKE, A. M.--FC12
 WU, MING--FB4

X

XIE, WEI--TG13
 XU, L.-W.--TA8

Y

YAMADA, C.--PA4
 YAMAMOTO, S.--TG8
 YAMANOUCHI, K.--RC8
 YAN, W.-B.--PB3, PB7
 YANG, B. C.--WH8
 YARON, DAVID--RA5, RA6
 YOSHINO, K.--TB7, TB8
 YU, G.-S.--WG1
 YU, LIAN--TG11, FB13, FB14

Z

ZAGANO, C.--TC5
 ZELLMER, R. J.--RG5
 ZEMKE, W. T.--TG1
 ZHANG, J.--PB10
 ZHAO, Z. --TC10
 ZHAO, Z. Q.--FC5
 ZHENG, X.--ME4, ME5, TG5
 ZHILINSKI, B. I.--WA3
 ZWART, E.-ME8
 ZWIER, T. S.--WH4, WH5, WH6

46TH OHIO STATE UNIVERSITY INTERNATIONAL SYMPOSIUM ON MOLECULAR SPECTROSCOPY

JUNE 17-21, 1991

| MONDAY JUNE 17TH 8:45 AM - NOON | TUESDAY JUNE 18TH 8:30 AM - NOON | WEDNESDAY JUNE 19TH 8:45 AM - NOON | THURSDAY JUNE 20TH 8:30 AM - NOON | FRIDAY JUNE 21ST 8:30 AM - NOON |
|--|--|---|---|---------------------------------------|
| MA. PLENARY SESSION H. M. PICKETT C. DEMUYNCK D. H. SUTTER COBLENTZ AWARD & LECTURE P. W. BOHN | | WA. PLENARY SESSION E. HERBST J. - P. CHAMPION B. J. ZHILINSKII N. C. HANDY | | |
| | TA. INFRARED (TECH. & IONS) L. N. SINITSIN | | RA. INFRARED S. URBAN | FA. MICROWAVE |
| | TB. ELECTRONIC (DIATOMICS) | | RB. ELECTRONIC | FB. LASER SPECTRA |
| | TC. VIBRATIONAL ANALYSIS | | RC. VARIOUS | FC. ENERGY TRANSFER |
| AUDITORIUM INDEPENDENCE HALL | | | | |
| ROOM 1153 PHYSICS LAB | | | | |
| ROOM 1009 PHYSICS LAB | | | | |
| ROOM 1005 PHYSICS LAB | | | | |

1:30 PM - 5:00 PM

| ME. MOLECULAR BEAM | TE. MOLECULAR BEAM | WE. C ₆₀ SEMINAR R. F. CURL W. KRATZSCHMER R. M. FITZER H. W. KROTO P. BERNATH | RE. MICROWAVE A. F. KRUPNOV | |
|------------------------------------|---|--|--------------------------------|--|
| MF. INFRARED | TF. HYDROGEN (SOLID & GASEOUS) TF. IR & AB INITIO | WF. INFRARED | RF. INFRARED | |
| MG. MATRIX | TG. ELECTRONIC (SMALL) | WG. CIRCULAR DICHROISM | RG. ELECTRONIC (THEORY) | |
| | | WH. VARIOUS | | |
| ROOM 1153 PHYSICS LAB | | | | |
| ROOM 1009 PHYSICS LAB | | | | |
| ROOM 1005 PHYSICS LAB | | | | |
| ROOM 1008 EVANS CHEMICAL LAB | | | | |